Physics Lib.

SEP 25 1947

REGISTERED No. M 3121

PROCEEDINGS

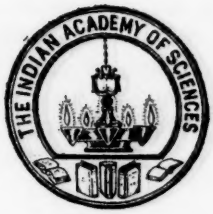
OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXVI] *SECTION A* [No. 1

JULY, 1947



Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

STUDIES ON SOILS

Part III. On the Effect of Concentration of Some Salts in Aqueous Solution on Capillary Ascent, Dispersion and Associated Phenomena in the Black Cotton Soil

By L. A. Ramdas and A. K. Mallik

(Agricultural Meteorology Section, Meteorological Office, Poona)

Received April 22, 1947

1. Introduction

In Parts I and II[1, 2] of this series the authors have discussed the results of a series of experiments on some properties of the black cotton soil. It was found that salts, the solutions of which move less freely through the soil than pure water, caused swelling of the layer of colloidal material with which the particles of black cotton soil are coated. In a later note[3] it was shown that for sodium carbonate, as the concentration of the solution was increased from 0 per cent. (water) to about 0·03 per cent., there was an increase in the capillary movement and that the well-known impermeability of the soil in the presence of sodium carbonate was seen only when the concentration was increased beyond the above optimum value. It was suggested that this 'optimum' may be due to the slight constriction of the capillaries between soil particles due to incipient swelling of their colloidal coatings and the consequent increase in the upward pull. At higher concentrations further swelling chokes up the pore space in the soil and causes impermeability.

In the present paper we describe the results of further experiments on the capillary ascent of different concentrations of solutions of lithium carbonate, sodium carbonate, oxalic acid, lithium oxalate and sodium oxalate. In the case of sodium carbonate it has been possible to study the phenomenon over a very wide range of concentrations owing to the very large solubility of this salt in water. Over the same range of concentration, the development of cracks in the black cotton soil on being mixed with the solution and then allowed to dry has been studied. The volume of the sediment when similar quantities of soil are shaken with the same volume of solutions of different concentration and then allowed to settle has been measured. The results obtained are discussed in the following sections.

2. The Ascent of Solutions of Different Concentrations of Some Salts in a Column of Black Cotton Soil

The method used has already been described in detail in the earlier papers of this series and can be stated briefly as follows:—Air dry soil passed through a 1 mm. sieve is packed in glass tubes the lower ends of which are closed by pieces of muslin. The soil is packed in the tubes uniformly. The tubes are then dipped in the solutions with the muslin covered ends a little below the surface of the liquid. The heights of the wetted column (which is easily seen, due to the darkening of the soil on wetting) were recorded at suitable time intervals. The different salts experimented with are lithium carbonate, sodium carbonate, oxalic acid, lithium oxalate and sodium oxalate. The results obtained with the different concentrations of aqueous solutions of the abovementioned salts and oxalic acid are given in Tables I to V respectively.

Table I

Capillary ascent in black cotton soil of lithium carbonate solutions of different concentrations, in cm.

Time	Concentration of solution in per cent. (grammes of Li_2CO_3 in 100 c. c. of water										
	0 water	0·005	0·01	0·015	0·02	0·03	0·05	0·10	0·20	0·30	0·50
Hrs.											
1 ..	3·9	4·0	4·2	4·2	4·7	4·3	3·8	1·6	0·0	0·0	There was absolutely no ascent even after 50 hrs.
3 ..	8·2	8·4	8·7	8·8	9·3	8·8	6·3	2·6	0·5	0·0	
8 ..	14·9	15·2	15·7	16·0	16·6	15·2	9·0	3·6	1·2	0·1	
15 ..	20·0	20·3	21·0	21·1	22·4	19·7	10·4	4·1	1·5	0·5	
24 ..	24·2	24·8	25·8	26·7	27·5	22·9	11·6	4·8	1·6	0·8	
33 ..	27·1	28·0	29·3	30·5	30·9	25·0	12·6	5·1	1·6	0·8	
50 ..	31·3	32·7	34·2	35·5	35·9	27·5	13·9	5·8	1·7	0·8	

Table II

Capillary ascent in black cotton soil of sodium carbonate solutions of different concentrations, in cm.

Time	Concentration of solution in per cent. (grammes of Na_2CO_3 in 100 c.c. of water)									
	0 water	0·01	0·02	0·03	0·04	0·05	0·125	0·25	0·50	1·00
Hrs.										
1 ..	4·2	4·6	5·2	5·3	5·6	5·6	4·7	2·5	1·7	1·9
3 ..	8·9	9·5	10·5	10·5	11·0	10·3	6·9	3·4	2·5	2·3
8 ..	16·2	17·3	18·7	18·9	19·3	18·5	9·2	4·5	3·1	2·5
14 ..	21·8	22·7	24·4	24·7	24·9	23·6	10·4	4·9	3·5	2·9
24 ..	28·8	29·9	31·7	32·3	31·7	28·0	12·0	5·4	3·9	3·1
33 ..	32·9	34·5	36·5	36·9	35·7	33·5	12·7	5·9	4·3	3·3
48 ..	39·5	41·2	43·3	43·8	41·2	36·3	13·5	6·3	4·5	3·3

TABLE III

Capillary ascent of black cotton soil of oxalic acid solutions of different concentrations, in cm.

Time	Concentrations of solutions in per cent. [grammes of $(COOH)_2 2H_2O$ crystals in 100 c.c. of water]								
	0 water	0·05	0·10	0·20	0·50	1·00	2·00	3·00	5·00
Hrs.									
1 ..	4·2	4·3	5·0	5·0	4·5	2·8	1·9	0·9	0·4
3 ..	8·7	9·4	10·2	10·3	9·4	5·8	4·1	2·6	1·7
8 ..	15·5	17·4	19·2	18·4	16·8	10·4	7·5	5·2	3·7
14 ..	20·6	23·9	26·0	25·0	22·6	15·0	11·0	7·8	5·7
24 ..	26·8	31·3	33·8	32·6	29·9	20·8	15·2	11·0	7·9
33 ..	30·8	35·8	38·6	37·3	34·6	24·5	17·7	12·9	9·6
48 ..	36·3	42·5	45·7	44·3	41·5	28·7	20·9	15·3	10·7

TABLE IV

Capillary ascent in black cotton soil of lithium oxalate solutions of different concentrations, in cm.

Time	Concentration of solutions in per cent. (grammes of $Li_2C_2O_4$ in 100 c.c. of water)									
	0 water	0·005	0·01	0·02	0·03	0·05	0·10	0·20	0·30 Inter-polated	0·50
Hrs.										
1 ..	4·7	5·0	5·6	5·4	4·5	4·2	3·3	2·7	2·0	1·3
3 ..	9·0	9·4	10·2	9·9	9·0	6·0	5·2	4·1	3·7	3·2
8 ..	17·4	18·0	19·0	17·3	16·2	8·1	7·3	5·3	4·4	3·5
14 ..	23·4	24·6	25·6	24·1	22·0	9·4	8·4	5·9	4·7	3·6
24 ..	30·2	30·4	31·5	31·1	27·3	11·6	9·1	6·1	5·1	4·0
33 ..	34·2	35·2	36·2	35·3	28·6	13·0	9·9	6·8	5·4	4·0
51 ..	39·4	40·0	41·2	40·0	30·5	14·2	11·0	8·1	6·1	4·2

TABLE V

Capillary ascent in black cotton soil of sodium oxalate solutions of different concentrations, in cm.

Time	Concentration of sodium oxalate solutions in per cent. (grammes of $Na_2C_2O_4$ per 100 c.c. of water)					
	0 water	0·01	0·03	0·05	0·20	0·50
Hrs.						
1 ..	3·3	4·1	3·9	4·1	3·8	3·1
3 ..	7·4	8·1	8·0	8·2	7·7	4·7
8 ..	14·1	14·7	14·4	14·7	12·0	6·2
14 ..	19·4	19·7	19·5	19·7	14·0	7·0
24 ..	25·5	25·9	25·5	25·3	15·9	7·9
33 ..	30·1	30·1	29·4	28·7	16·9	8·3
48 ..	36·2	36·1	35·4	33·1	18·5	9·1

The results are also shown graphically in Figs. 1 to 5. An examination of the above data shows:—

(1) The capillary ascent increases with the concentration of the solution up to an optimum value beyond which there is a rapid decrease. This is true for all the solutes experimented with except sodium oxalate. The

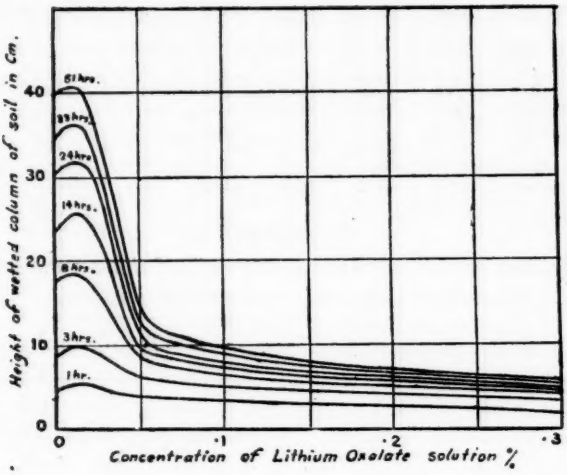


FIG. 1

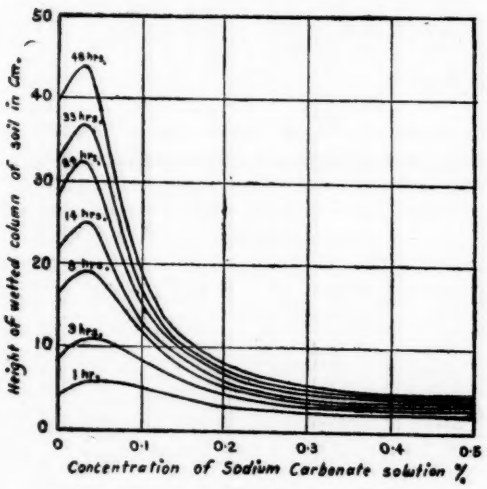


FIG. 2

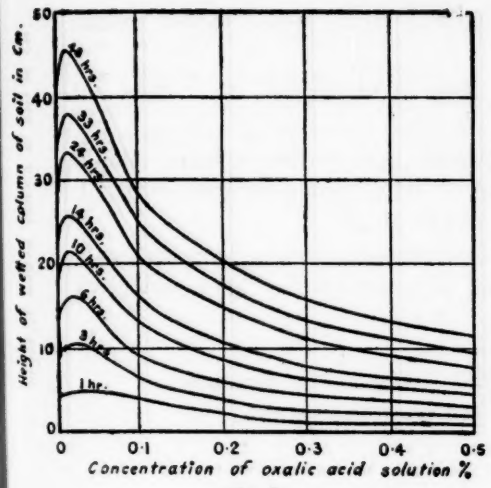


FIG. 3

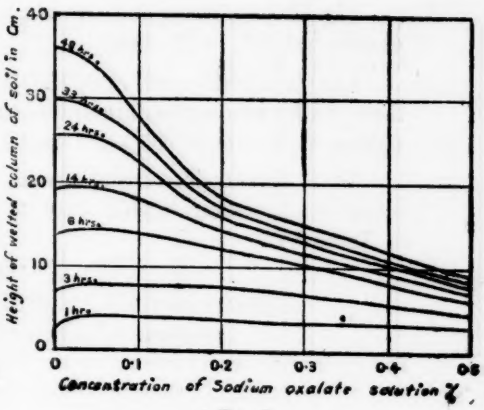


FIG. 5

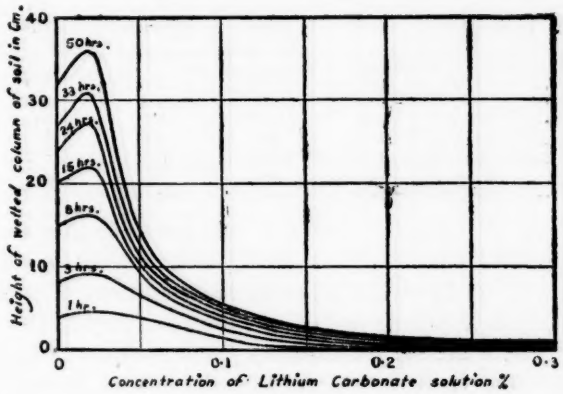


FIG. 4

optimum concentration at which the rise of the solution is maximum is, however, different for the different substances. This concentration, as seen above, is 0·02 per cent. for lithium carbonate, 0·03 per cent. for sodium carbonate, 0·01 per cent. for lithium oxalate and 0·10 per cent. for oxalic acid. As suggested in an earlier note,[3] this is probably due to the constriction of the soil capillaries caused by the incipient swelling of the colloidal coatings of the soil particles at very low concentrations, and the consequent increase in the upward pull. At higher concentrations further swelling causes choking up of the pore space in the soil resulting in impermeability.

The absence of an ' optimum ' concentration in the case of sodium oxalate requires further investigation.

(2) The concentration at which there is maximum ascent does not change sensibly with time.

(3) Considering the optimum concentrations for the different solutes, these can be arranged as lithium oxalate (0·01%), lithium carbonate (0·02%), sodium carbonate (0·03%) and oxalic acid (0·10%).

Some further interesting results were obtained with sodium carbonate using concentrations higher than those discussed above. These are given in Table VI.

TABLE VI

Capillary ascent in black cotton soil of sodium carbonate solutions of different concentrations, in cm.

Time	Concentration of solutions in per cent. (grammes of Na_2CO_3 in 100 c.c. of water)					
	0 water	2·00	3·00	6·25	12·50	25·00
Hrs.						
1 ..	4·0	0·4	0·5	0·7	1·4	4·5
3 ..	8·6	0·5	0·7	1·1	4·4	11·7
8 ..	16·0	0·8	1·3	2·7	9·2	21·3
14 ..	21·5	1·3	2·2	4·3	13·3	23·8
24 ..	28·4	1·9	3·0	6·8	19·5	26·1
33 ..	32·6	2·4	4·2	8·7	22·7	26·8
50 ..	39·3	2·5	5·1	10·5	25·2	27·2
				Wetted soil became jet black		

The ascent in 24 hours for different concentrations of sodium carbonate solutions, from 0 (water) to 25%, is shown in Fig. 6. The chief points of interest in Fig. 6 are (1) the capillary ascent increases with the increase of the concentration up to 0·03%, (2) with the further increase in the concentration there is a rapid fall in the ascent with a minimum value at 2%, (3) when the concentration is further increased the capillary ascent increases again giving a secondary maximum at a concentration of 25% (almost saturated solution). The initial increase in the ascent up to 0·03% and the later fall up to 2% have already been discussed earlier. It was noticed that the soil column wetted by the higher concentrations of the solution turned black after some time. This shows that some organic compound like humus in the soil is getting dissolved in the concentrated solution of sodium carbonate thus changing the colour of the wet soil column to black. The increase in the capillary ascent in higher concentrations, must therefore be due to

the colloidal coatings of the soil particles getting dissolved in the solution. The soil particles tend to behave like sand once the colloidal coating is dissolved, so that a concentrated solution of sodium carbonate rises through the soil even at a faster rate than water initially (as through sand) although, ultimately, the rise is more in the case of water.

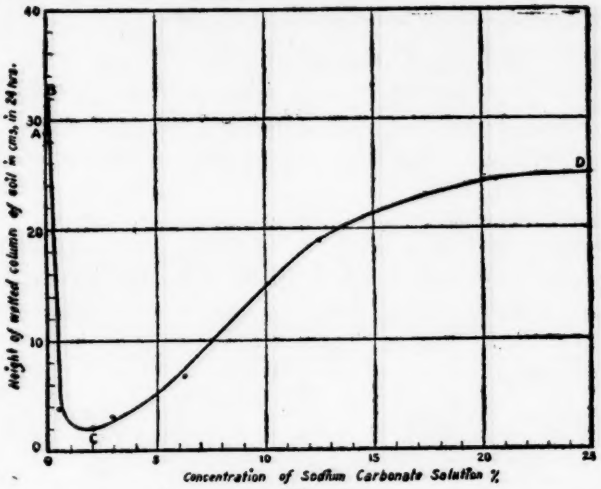


FIG. 6

3. THE EFFECT OF CONCENTRATION OF SODIUM CARBONATE SOLUTION ON THE DEVELOPMENT OF CRACKS IN THE SOIL

Samples of black cotton soil weighing 100 grammes were mixed with 60 c.c. of sodium carbonate solutions of different concentrations and the pastes so formed were allowed to dry. The soil layers developed the well-known cracks (see Fig. 7). It was found that cracks developed only in the range of concentrations from 0 to 5 per cent. The width of the cracks formed increased to a maximum at the concentration of 3%. No deep cracks appeared in concentrations above 5%, although superficial cracking was present in 7 and 8 per cent. concentrations. Between 4 per cent. and 8 per cent., the soil mass contracted *en masse* on drying and a black layer appeared on the surface. This contraction also decreased from 4 to 8 per cent. At higher concentrations the soil particles, being deprived of the cementing action of humus, have no tendency to form lumps but remain powdery and porous like sand. It is reasonable to expect that maximum cracking should occur at the concentration (or rather at that value of the ratio of soil to salt) at which the swelling on wetting and the subsequent shrinking on drying are both maximum. The cracked layers increase in their hardness with the

concentration, the maximum hardness being at 3%. At higher concentrations the dried mass was quite friable. This is probably due to the fact that, as explained above, at higher concentrations organic compounds (of the nature of humus) which serve as the binding material, are getting dissolved in the concentrated sodium carbonate solution with the result that the soil particles left behind behave like particles of sand.

4. The Effect of Different Concentrations of Some Salts in Aqueous Solutions on the Swelling and Dispersion of Soils

In this experiment 3 gramme samples of the local black cotton soil were shaken for about 2 minutes with 100 c.c. of different concentrations of solutions of (1) oxalic acid, (2) lithium oxalate, (3) sodium oxalate, (4) lithium carbonate and (5) sodium carbonate. The mixture was allowed to settle in 100 c.c. measuring jars. After complete settling (*i.e.*, after 2 days) the volumes of the sediments in the different concentrations of the different salts were recorded. Four replications of each concentration of each salt were tried. The mean values of the volumes of sediments in the different concentrations of the five salts per gramme of soil, are given in Table VII.

Table VII

Swelling of soil

Concentration of solution in per cent. (gm. per 100 c.c. of distilled water)	Volume of sediments in c. c. per gm. of soil				
	Oxalic acid	Lithium oxalate	Sodium oxalate	Lithium carbonate	Sodium carbonate
0·0 (distilled water)	1·8	1·8	1·8	1·8	1·8
0·1	2·0	3·2	2·3	3·7	2·2
0·2	2·5	4·7	3·3	5·0	2·3
0·3	2·7	5·5	4·2	6·0	2·7
0·5	3·0	6·0	4·7	6·7	3·0
		6·5*			
1·0	3·3	6·0	4·0	5·8	3·7
2·0	4·6	4·3	3·3		2·8
4·0	5·3	3·0	2·3		2·0
6·0	5·7				1·7
8·0	6·0				1·6
10·0		*Refers to			1·5
20·0		0·7%			1·3

It was also noticed that at higher concentrations of all the chemicals, except in the case of oxalic acid, the supernatant liquid became dark coloured, the intensity of colour increasing with concentration. It will be seen from Table VII, that in all cases except in the case of oxalic acid the volume of

sediments increases with concentration up to a certain critical concentration beyond which the volume of sediments decreases. This is apparently due to the fact that these salts cause a swelling of the soil particles increasing with concentration (*i.e.*, salt to soil ratio). The decrease of the sediments at higher concentrations is due to the colloidal coating of the soil particles getting dissolved in the solutions. This dissolving action also increases with concentration. The dark colour of the supernatant liquid at higher concentrations noted above, confirms this view. Thus the results of this experiment supports the hypothesis put forward in Section 2 above, that with the increase of concentration the volume of soil particles increases resulting in a greater capillarity and then further swelling chokes up the pore space reducing greatly the capillary ascent. As the concentration is further increased the colloidal coating of soil particles having gone into solution, the soil particles behave just like sand so that the capillary ascent increases somewhat. Unlike other salts, as mentioned above, the supernatant liquid in the case of oxalic acid is clear except for the presence of fine yellow precipitates, presumably calcium oxalate, even when the solution is saturated. In the case of oxalic acid the dissolving action appears to be absent so that there is no decrease in the volume of sediments beyond an optimum concentration.

5. Some Applications of the Findings

The importance of the above results in dealing with problems connected with soil is obvious. There is an optimum concentration (1%) of sodium carbonate solution at which the auto-dispersion of the black cotton soil (*e.g.*, for the mechanical analysis) will be maximum. Similarly, the influence of concentration on phenomena like crack formation, swelling and permeability is noteworthy. It is the practice amongst the irrigation engineers to give a lining of sodium carbonate to the sides of the irrigation canals to prevent seepage. The above results indicate that for the lining to be most effective, the concentration of the sodium carbonate in the soil layers at the sides of the canals should be maintained at an optimum value of about 2 per cent. in the black cotton soil tracts.

6. Capillary Movement in Relation to Other Physical Properties of the Soil

A comprehensive discussion of the capillary movement of water through a porous medium like the soil will be found in Keen's well-known book[4] (Ch. III). In Keen's discussion soil particles are idealised as spheres and the theory has been refined suitably taking into consideration the exact shape and cross-section of the free space between uniform spheres packed

closely. In the present paper we are dealing with a class of phenomena where capillary ascent is affected by swelling of colloidal cover of particles and at high concentrations by chemical action and dissolution of the colloidal fraction resulting in a restoration of permeability. It is sufficient for our purposes to examine the capillary ascent in such a complex medium on the basis of the simpler theory (outlined by Green and Ampt and quoted on pages 94 to 96 of Keen's book). In the case where water is rising vertically in a soil column under the influence of capillarity against hydrostatic pressure, if the lower end be just in contact with the water surface then we have

$$\frac{dl}{dt} = \frac{P}{S}\frac{K - l}{},$$

where P = Permeability of the soil,

S = pore space,

K = capillary force acting on the moving boundary of the water and

l is the height of the wet soil column above the water surface.

On integration we get

$$\frac{Pt}{S} = K \log \frac{K}{K - l} - l$$

or

$$\frac{P}{S} = \frac{K \log K/(K - l) - l}{t}.$$

We may try to estimate P/S at different times after the start of capillary ascent and for different concentrations by substituting the data given in Tables I to V in the above equation. It will be necessary to do this by trial, choosing a value of K such that the computed value of P/S for any one concentration of the ascending fluid will be constant for different hours. The results so obtained are given in Table VIII for the case of sodium carbonate. In this table the computed mean values of P/S corresponding to the values of K which give the best fit for the P/S ratios are given. The following tentative conclusions may be drawn from Table VIII.

(1) The capillary force which depends on the effective size and number of the capillaries in the soil column remains more or less steady at about 400 in the concentration range 0 to 0·05%. Thereafter owing to the clogging up of the pore space the capillaries tend to be obliterated so that there is a rapid decrease of K from 0·05 to 1·00%. With further increase of concentration chemical action sets in and the colloidal material gets

dissolved so that the number of capillaries rapidly increases. Beyond the 2% concentration, therefore, the permeability of the soil increases rapidly. The values of K also increase correspondingly.

(2) P/S which is the ratio of permeability to the pore space would tend to remain constant if the changes in P and in S are proportionate. Actually, however, there is a slight increase with concentration in the range 0 to 1·0%, due presumably to the decrease in pore space being more rapid than that of permeability. When chemical action sets in at a concentration higher than 1%, there is an abrupt decrease (*e.g.*, at 2% concentration) in P/S due to the rapid increase in the pore space S. With further increase of concentration P/S attains rapidly a value more or less similar to that in the case of a dilute solution. It appears that there is a slight lag between changes in S and those in P.

TABLE VIII

Average value of P/S and K at various concentrations of sodium carbonate

	Concentration of sodium carbonate solution in per cent. (gm. per 100 c.c. of distilled water)														
	0 water	0·01	0·02	0·03	0·04	0·05	0·125	0·25	0·50	1·00	2·00	3·00	6·25	12·50	25·00
P/S ..	1·21	1·21	1·55	1·99	1·48	1·36	3·04	3·25	3·24	5·48	0·19	0·33	0·50	2·01	2·44
K ..	409	411	430	434	430	397	60	15	8	5	9	16	40	80	200

7. SUMMARY AND CONCLUSION

The present paper describes the effect of substances like lithium carbonate, sodium carbonate, oxalic acid, lithium oxalate and sodium oxalate in aqueous solution on (*a*) capillary ascent through soil columns, (*b*) formation of cracks in soil layers, and (*c*) swelling and dispersion of soils. The experiments described refer to the black cotton soil. It is shown that these phenomena are profoundly modified by the concentration of these substances in solution.

While these substances increase capillary ascent in traces, there is a rapid decrease in permeability due to the swelling of the colloidal fraction with increase of concentration; at still higher concentrations chemical effects set in tending to dissolve the colloidal fraction and to restore the permeability. The tendency of soils mixed with the solution to develop the characteristic cracks on drying is observed to follow a similar sequence, the cracks increasing in size up to an optimum concentration and thereafter not forming at all owing to the dissolving action on the cementing colloidal material.

The swelling and dispersion of the soil also follow a similar sequence.

The bearing of these phenomena on the lining of canals with sodium carbonate to prevent seepage is also pointed out.

The effect of swelling on capillary ascent as controlled by P, the permeability and S, the pore space, at the different concentrations of sodium carbonate in aqueous solution is discussed.

In conclusion, it may be mentioned that experiments are now in progress to study the methods of restoring the permeability to a soil column rendered previously impermeable by the action of sodium carbonate. The results of these interesting experiments will be discussed in the next part of this series.

Our best thanks are due to the Director-General of Observatories for providing the necesssary facilities for this investigation.

References

1. Ramdas, L. A., and Mallik, A. K. .. *Proceedings of the Indian Academy of Sciences*, 1942, **16**, No. 1.
2. ———— .. *Ibid.*, 1942, **16**, No. 1.
3. ———— .. *Current Science*, February 1944.
4. Keen, B. A. .. *The Physical Properties of Soils*, 1931.

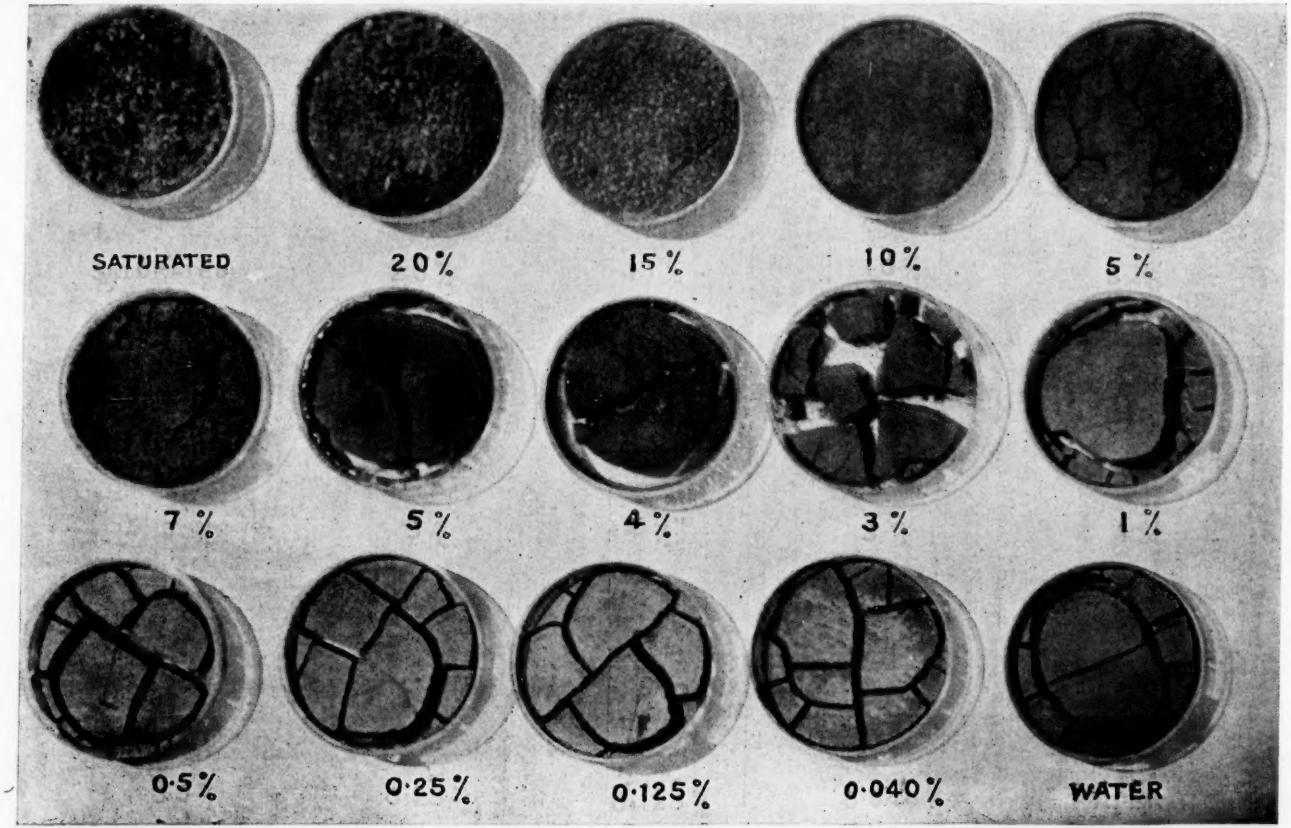


FIG. 7

Development of cracks in the black cotton soil when it is mixed with different concentrations of sodium carbonate solution and then dried.

NUCLEAR OXIDATION IN THE FLAVONE SERIES

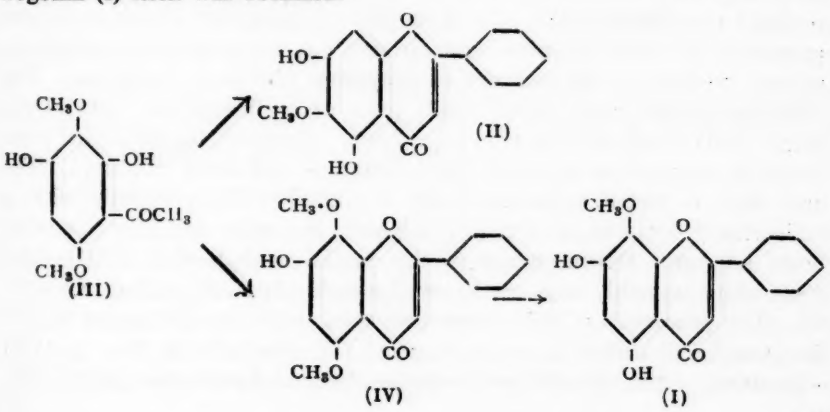
Part V. A New Synthesis of Wogonin

By K. Venkateswara Rao, K. Visweswara Rao
and T. R. Seshadri, F.A.Sc.

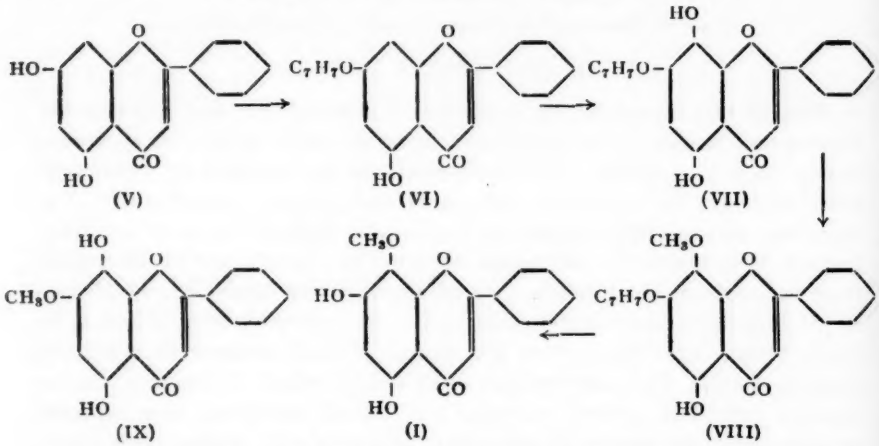
(From the Department of Chemistry, Andhra University, Waltair)

Received May 12, 1947

In Part II[1] was described the synthesis of norwogonin and isowogonin. Norwogonin has not so far been found to occur free in nature, but its monomethyl ether is wogonin. This compound was first isolated by Takahashi[2] from the roots of *Scutellaria baicalensis* and named 'Scutellarin'. The name was subsequently changed to wogonin by Shibata[3] in order to distinguish it from a different compound obtained by Molisch and Goldschmidt[4] from the roots of *S. altissima*. Its constitution was established by Hattori as 5:7-dihydroxy-8-methoxyflavone[5] (I). Its synthesis was effected by Shah, Mehta and Wheeler[6] in the course of their attempt to synthesise oroxylin-A (II). The condensation of 2:4-dihydroxy-3:6-dimethoxy-acetophenone (III) with sodium benzoate and benzoic anhydride was expected to take the same course as the condensation of this ketone with anisic anhydride and sodium anisate[7] with partial demethylation and subsequent ring closure to yield the 6-methyl-ether of baicalein (II). Unexpectedly the reaction proceeded in the normal way forming wogonin-monomethyl ether (IV). From this by partial demethylation with aluminium chloride wogonin (I) itself was obtained.

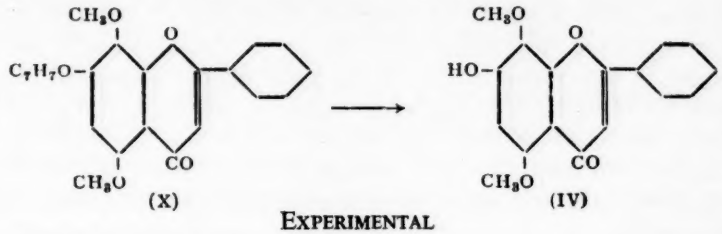


Though 8-methyl ethers of the type of wogonin are not well known, they do not seem to be so rare. Tambuletin[8] which has recently been isolated from tambul seeds seems to belong to this category. In order to render the study of these new compounds more easy, the application of the recent discovery of facile nuclear oxidation in flavones has been made for the synthesis of wogonin. The method works quite satisfactorily and is capable of wide application. The scheme adopted is represented below:



The benzylation of chrysin (V) was carried out earlier by Gulati and Venkataraman[9] using various conditions. They found that 7-O-benzyloxy-6-benzyl chrysin was the only product though in the parallel case of 5:7-dihydroxy-2-methyl-chromone the simple 7-benzyloxy-compound was obtained under those conditions. It has now been possible to prepare the required monobenzyl-ether (VI) of chrysin by using just over a molecular proportion of benzyl chloride and carrying out the reaction in anhydrous acetone medium in the presence of anhydrous potassium carbonate. The oxidation of the benzyl ether takes place easily though the yield of the quinol (VII) is not so good as in other cases. However, the unreacted ether could be recovered in an almost pure condition and could be reused. The next stage is partial methylation and this is effected conveniently with a molecular proportion of dimethyl sulphate, the more resistant 5-position being left out. Debenzylation of this partial methyl ether (VIII) takes place quite smoothly with acetic and hydrochloric acids yielding wogonin (I). The properties of this compound agree with the description in the literature.[3] It differs from isowogonin[1] (IX) markedly in the reactions with alkali, ferric chloride and *p*-benzoquinone and resembles chrysin (V).

Complete methylation of (VII) with excess of dimethyl sulphate yields the dimethyl ether (X) which after debenzylation forms wogonin-5-methyl ether (IV) readily. Further methylation of (I) and (IV) give rise to 5: 7: 8-trimethoxy flavone identical with the synthetic sample obtained by Sastri and Seshadri.[10] All these transformations add further support to the constitution of the monobenzyl-ether of chrysin (VI).



EXPERIMENTAL

7-Benzyloxy-5-hydroxy-flavone (VI):

A solution of chrysin (V) (1 g.) in anhydrous acetone (100 c.c.) was treated with freshly distilled benzyl chloride (0·52 c.c.) and anhydrous potassium carbonate (5 g.). After refluxing the contents for 20 hours, the solvent was distilled off and the residue treated with water (200 c.c.). The undissolved yellowish brown solid was filtered, washed with petroleum ether followed by water and the aqueous filtrate preserved (F). The solid residue was the benzyl ether; yield 0·6 g. On crystallisation from acetone containing a few drops of glacial acetic acid it separated out in the form of glistening pale brown thin elongated rectangular plates melting at 173–75°. (Found: C, 76·8; H, 5·0; $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%.) It was sparingly soluble in alcohol, acetone or ethyl acetate. In alcoholic solution it gave a deep reddish brown colour with ferric chloride. It was insoluble in aqueous sodium hydroxide and on boiling the mixture, the solid turned deep yellow.

On acidifying the brown aqueous filtrate (F) a cream-coloured solid separated out which was filtered and washed with water. When recrystallised from alcohol it yielded pure chrysin (0·3 g.).

5: 8-Dihydroxy-7-benzyloxy-flavone (VII):

To a stirred solution of 5-hydroxy-7-benzyloxy-flavone (VI) (1 g.) in a mixture of pyridine (35 c.c.) and aqueous potassium hydroxide (0·9 g. in 20 c.c.) was added dropwise a solution of potassium persulphate (1·5 g. in 50 c.c. of water) during the course of 2 hours. After keeping the deep brown solution for 24 hours it was slightly acidified when a pale brown precipitate was thrown down. It was filtered and washed with water. It

was found to be almost pure 7-benzyloxy-5-hydroxy-flavone; recovery 0·6 g. The filtrate was twice extracted with ether and the clear aqueous layer was treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and heated in a boiling water-bath for 30 minutes. A yellow crystalline solid separated out in the course of the heating. After cooling it was filtered and washed with water; by extracting the filtrate with ether some more of the substance was obtained. Yield 0·2 g. On crystallisation from a mixture of ethyl acetate and benzene it separated out in the form of bright golden yellow narrow rectangular plates melting at 220–21°. (Found: C, 72·9; H, 4·3; $C_{22}H_{16}O_5$ requires C, 73·3; H, 4·4%.) It was sparingly soluble in alcohol, ethyl acetate and ether. In alcoholic solution it gave with ferric chloride a pale green colour which quickly changed to deep brown. It dissolved in aqueous sodium hydroxide to a deep reddish brown solution.

8-*Methoxy*-7-*benzyloxy*-5-*hydroxy-flavone* (*VIII*):

A solution of 5: 8-dihydroxy-7-benzyloxy flavone (VII) (0·4 g.) in anhydrous acetone (25 c.c.) was treated with dimethyl sulphate (0·1 c.c.) and potassium carbonate (2 g.). After refluxing for 6 hours the solvent was distilled off and the residue treated with water (50 c.c.). The undissolved solid was filtered and washed with water. After crystallisation from acetone it separated out in the form of pale yellow soft woolly needles melting at 208–10°. (Found: C, 73·9; H, 5·0; $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%.) It was very sparingly soluble in alcohol and acetone but more easily in benzene. In alcoholic solution it gave a stable green colour with ferric chloride. It was insoluble in alkali even on heating.

8-*Methoxy*-5: 7-*dihydroxy flavone*: *Wogonin* (I):

Concentrated hydrochloric acid (3 c.c.) was added to a solution of 8-methoxy-7-benzyloxy-5-hydroxy-flavone (VIII) (0·15 g.) in glacial acetic acid (10 c.c.) and the solution kept in a boiling water-bath for 1 hour. Water (100 c.c.) was then added and the yellow solid that separated out was filtered off and washed with water. Crystallisation from a mixture of ethyl acetate and benzene yielded bright yellow glistening stout spear-shaped crystals melting at 200–02.° (Found: C, 67·7; H, 4·5; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.) It was easily soluble in alcohol, ethyl acetate and acetone but sparingly in benzene. In aqueous sodium carbonate and sodium hydroxide it readily dissolved to a bright golden yellow solution. In alcoholic solution it gave a greenish brown colour with ferric chloride and it was unchanged on adding excess of the reagent. It did not react with *p*-benzoquinone.

5: 8-*Dimethoxy-7-benzyloxy-flavone* (*X*):

A solution of 7-benzyloxy-5 : 8-dihydroxy-flavone (VII) (0·15 g.) in anhydrous acetone (20 c.c.) was refluxed with dimethyl sulphate (0·2 c.c.) and potassium carbonate (2 g.) for 6 hours. The solvent was distilled off, the residue treated with water and the pale brown solid that remained behind was filtered off and washed with water. Crystallisation from a mixture of benzene and petroleum-ether furnished the compound in the form of colourless prismatic needles melting at 160–61°. (Found: C, 73·9; H, 5·1; $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%.) It was insoluble in aqueous alkali and did not give any colour with ferric chloride.

5: 8-*Dimethoxy-7-hydroxy-flavone* (*IV*):

Concentrated hydrochloric acid (2 c.c.) was added to a solution of 5: 8-dimethoxy-7-benzyloxy flavone (X) (0·1 g.) in glacial acetic acid (5 c.c.). After keeping the mixture in a boiling water-bath for 1 hour and finally heating it to boiling, it was cooled and diluted with water (50 c.c.). The light brown solid product was filtered, washed with water, dried and crystallised from absolute alcohol from which it separated in the form of almost colourless rhombohedral plates and needles melting at 285–87°. It was sparingly soluble in alcohol and other common organic solvents and readily dissolved in aqueous sodium hydroxide to a yellow solution. It was found to be identical with the sample obtained by Sastri and Seshadri[10] from 2: 4-dihydroxy-3: 6-dimethoxy-acetophenone by adopting the Baker Venkataraman procedure; the mixed melting point was undepressed.

Summary

Using the new discovery of facile nuclear oxidation in hydroxy-flavones, (1) wogonin and (2) its 5-methyl ether have been synthesised. Starting with 7-O-benzyl-chrysin, oxidation followed by partial methylation and debenzylation yields (1) and by complete methylation and debenzylation yields (2).

References

1. Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1947, **25**, 427.
2. Takahashi .. *Chem. Zentr.*, 1889, **2**, 620.
3. Shibata *et al.* .. *Acta Phytochim.*, 1923, **1**, 105.
4. Molisch and Goldschmidt .. *Monatsh.*, 1901, **22**, 679.
5. Hattori .. *Acta Phytochim.*, 1930, **5**, 99.
6. Shah, Mehta and Wheeler .. *J. C. S.*, 1938, 1555.
7. Wessely and Moser .. *Monatsh.*, 1930, **56**, 97.
8. Balakrishna and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1947, **25**, 449.
9. Gulati and Venkataraman .. *J. C. S.*, 1936, 268.
——, Seth and Venkataraman .. *Ibid.*, 1934, 1765.
10. Sastri and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1946, **24**, 243.

NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part VI. A New Synthesis of Calycopteretin and 6 : 8-Dihydroxy-quercetin

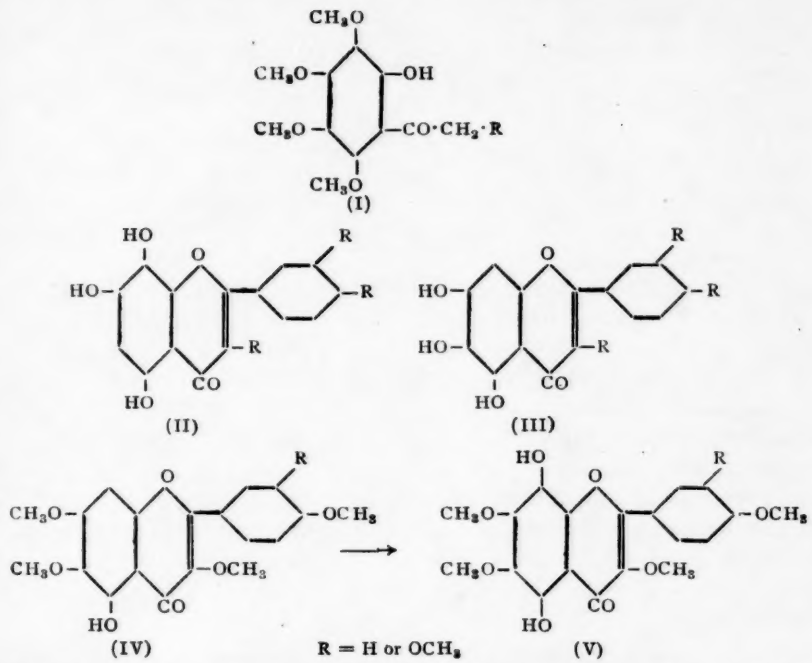
By S. Rajagopalan, K. Visweswara Rao and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University, Waltair)

Received May 12, 1947

5 : 6 : 7 : 8-Hydroxy-flavones and flavonols form an important group of highly hydroxylated compounds and several of them and related substances occur in nature. In the earlier synthesis of these compounds, suitable derivatives (methyl ethers) of pentahydroxy-acetophenone (I) were employed and the required flavone or flavonol molecule built up. Thus were synthesised nobiletin by Horii[1] and all the main flavonols of the calycopteretin series by workers in this laboratory.[2] An alternative method which is of interest from the point of view of biogenesis will be by nuclear oxidation of the appropriate lower member. In this connection these flavonols can be viewed in either of two ways, (1) as oxidation products of 5 : 7 : 8-hydroxy-flavones or flavonols (II) or (2) as oxidation products of 5 : 6 : 7-hydroxy-flavones and flavonols (III). Attempts made to oxidise 3 : 7 : 8 : 3′ : 4′-O-pentamethyl-gossypetin with a hydroxyl free in the 5-position under the ordinary conditions, were not successful; ortho oxidation does not seem to take place so readily. On the other hand, the isomeric quercetagetin-pentamethyl ether (IV, R = OCH_3) undergoes oxidation very readily and gives rise to a good yield of the corresponding quinol (V, R= OCH_3). Methylation of this yields the heptamethyl ether of 6 : 8-dihydroxy-quercetin and demethylation the free flavonol itself. For this purpose quercetagetin obtained from the flowers of *Tagetes erecta*[3] was employed and subjected to partial methylation using the correct quantities of dimethyl sulphate and potassium carbonate. In a similar manner the tetramethyl ether of nor-tangeretin (IV, R= H) was made from a synthetic sample[4] and this was subjected to oxidation. The quinol (V, R= H) on methylation yielded calycopterin dimethyl ether and on demethylation calycopteretin itself.

From the abovementioned results it would appear that compounds with the 5 : 6 : 7-arrangement of hydroxyl groups are the precursors of the compounds of the nobiletin and calycopterin series. In this connection may be mentioned the observation that nobiletin (5 : 6 : 7 : 8 type) is found in the peels of the Chinese Mandarin oranges,[5] *Citrus nobilis* and tangeretin



(5:6:7: type) in the closely related American Tangerines,[6] *Citrus nobilis deliciosa*.

Experimental

O-Pentamethyl-quercetagetin (*IV*, *R*= OCH_3):

A solution of quercetagetin (1·5 g.) in anhydrous acetone (75 c.c.) was treated with dimethyl sulphate (2·5 c.c.) and anhydrous potassium carbonate (10 g.). After refluxing for 6 hours, the solvent was distilled off and the residue treated with water when a yellowish brown solid was left behind. It was filtered, washed with water and crystallised twice from alcohol when it separated out in the form of pale yellow rectangular prisms melting at 158–60°. It was sparingly soluble in aqueous sodium hydroxide and gave a greenish brown colour with ferric chloride in alcoholic solution. The original alkaline filtrate on acidification did not give any appreciable amount of solid.

5:8-*Dihydroxy*-3:6:7:3′:4′-*pentamethoxy-flavone* (*V*, *R*= OCH_3):

O-Pentamethyl-quercetagetin (IV) (1 g.) was dissolved in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (0·8 g. in 25 c.c.) and

the clear yellowish brown solution was stirred and treated with aqueous potassium persulphate (1 g. in 50 c.c.) gradually during the course of two hours. The deep olive brown solution was allowed to stand for 24 hours and then rendered slightly acidic when a light brown precipitate was formed. It was filtered off and washed with water; yield 0·3 g. It was found to be almost pure pentamethyl quercetagetin. The filtrate was extracted twice with ether and the clear brown aqueous layer was treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and heated in a boiling water-bath for 30 minutes. After cooling, the yellow solid that separated out was filtered and washed with water; the filtrate furnished some more of the substance on extraction with ether; total yield 0·45 g. When crystallised from glacial acetic acid and subsequently from acetone it separated in the form of bright yellow narrow rectangular plates melting at 255–57°. (Found: C, 59·5; H, 5·2; $C_{20}H_{20}O_9$ requires C, 59·4; H, 4·9%.) It was very sparingly soluble in alcohol, ethyl acetate and acetone and moderately in hot glacial acetic acid. It readily dissolved in aqueous sodium hydroxide (5%) giving a deep red colour which faded considerably on shaking with air. In alcoholic solution with ferric chloride it gave a green colour which quickly changed to deep reddish brown. With *p*-benzoquinone in alcoholic solution a red colour was produced.

The dihydroxy-compound (0.1 g.) was methylated in acetone medium (25 c.c.) with dimethyl sulphate (0·2 c.c.) and potassium carbonate (2 g.). The methyl ether crystallised from a mixture of benzene and petroleum-ether in the form of colourless flat needles melting at 130–31° identical with a sample of 3: 5: 6: 7: 8: 3′: 4′-heptamethoxy-flavone obtained by the method of Seshadri and Venkateswarlu.[2]

5: 8-*Dihydroxy*-3: 6: 7: 4′-*tetramethoxy-flavone* (*V*, *R*= *H*):

The required O-tetramethyl-nor-tangeretin (IV, R= H) was obtained by the partial methylation of a synthetic sample of nor-tangeretin as described under quercetagetin.

A stirred solution of 5-hydroxy-3: 6: 7: 4′-tetramethoxy-flavone (IV, R = H) (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1 g. in 25 c.c.) was gradually treated with a solution of potassium persulphate (1·5 g. in 50 c.c.) during the course of two hours. The clear greenish brown solution was kept for 24 hours and just acidified when a pale brown precipitate of the unchanged substance separated out. It was filtered and washed with water. The filtrate was extracted twice with ether and the aqueous layer was heated on a boiling water-bath after the addition

of sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.). The yellow crystalline solid that separated out was filtered and washed with water. The filtrate on extraction with ether provided some more of the substance. Yield 0·4 g. On crystallisation from a mixture of ethyl acetate and petroleum-ether the compound separated out in the form of glistening golden yellow rectangular plates melting at 212–14°. (Found: C, 61·3; H, 5·1; $C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8%).

The above dihydroxy compound (0·2 g.) was refluxed for 6 hours in anhydrous acetone (25 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (2 g.). The solvent was distilled off, and the residue treated with water when the methyl ether separated out as a pale brown solid. It was purified by crystallising from a mixture of benzene and petroleum ether when it separated out as colourless rectangular plates melting at 133–34° alone or in admixture with an authentic sample of calycopterin-dimethyl ether.

Summary

It is shown that 5:6:7:8-hydroxy-flavonols (Calycopteretin series) can be made from 5:6:7-hydroxy-flavonols (quercetagetin series) by the nuclear oxidation of the 8-position. Quercetagetin and nor-tangeretin have thus been converted into 6 : 8-dihydroxy-quercetin and calycopteretin in good yields.

References

1. Horii .. *Br. Chem. Abs.*, 1941, **A ii**, 331.
2. Seshadri and Venkateswarlu *Proc. Ind. Acad. Sci.*, A, 1946, **23**, 192.
   Murti, Row and Seshadri .. *Ibid.*, **24**, 233.
   Sastri and Seshadri .. *Ibid.*, **24**, 238.
3. Rao and Seshadri .. *Ibid.*, 1941, **14**, 289.
4. Row and Seshadri .. *Ibid.*, 1946, **23**, 23.
5. Tseng .. *J. C. S.*, 1938, 1003.
6. Nelson .. *J. A. C. S.*, 1934, **56**, 1392.

EMISSION BANDS OF HALOGENS

Part V. Continuous Bands of Chlorine

By Putcha Venkateswarlu, M.Sc.
(*Physics Department, Benares Hindu University*)

Received December 16, 1946
[Communicated by Dr. R. K. Asundi, M.Sc., Ph.D. (London), F.A.Sc.]

Introduction

Cameron and Elliot[1] working with high frequency discharge have recorded eight continuous bands of chlorine of which two intense continua (2564 Å and 3063 Å) were previously recorded by earlier workers.[2] Later Singh and Adiga[3] also working with high frequency discharge, in a communication from this laboratory reported some new continuous bands in addition to those already reported by previous workers. Till now no explanation has been put forward for all these continuous emission bands. In a series of papers entitled 'Emission Bands of Halogens,' Parts I, II, III and IV which hereinafter will be called Papers I, II, III and IV, a number of diffuse bands have been recorded and explained for iodine and bromine.[4] The spectrum of bromine (Paper IV) consisting of groups of diffuse bands, is apparently similar to that of iodine (Papers I to III), but is, however, bodily displaced towards shorter wavelengths. Another striking difference in the two spectra is that whereas the component bands in different groups in the iodine spectrum are generally well separated from one another and appear somewhat like sequences, in bromine they merge into one another and in general each group in bromine appears as a broad continuous band superposed by different maxima. It appears that this tendency is developed still further in the case of chlorine where only continuous bands are recorded. Further, the spectrum of chlorine appears to be displaced towards shorter wavelengths with respect to that of bromine. Different groups in the case of iodine and bromine are explained as arising in stable initial states and having for their final levels different repulsive states. As the component bands in all the groups are well separated in iodine, the repulsive states will have nearly flat potential energy curves, whereas in bromine they will have somewhat steep potential energy curves as the component bands in different groups merge into one another. The repulsive states in iodine and bromine are attributed to just those electronic terms that are theoretically possible. An explanation exactly similar to that given for iodine and bromine spectra will satisfactorily explain all the continuous bands of chlorine where the repulsive states will be still more steep. The present paper deals with this explanation. Experimental details and wavelengths of the maxima of the continuous bands are also given.

Experimental Details

A glass tube about 25 cm. long and 1·6 cm. diameter is fitted with two internal aluminium electrodes at about 15 cm. apart. Two clear quartz windows are attached to the two ends of the discharge tube. One side of the discharge tube is connected through a stopcock to a side tube containing cupric chloride. The side tube is fitted in an improvised small electric furnace. The other side of the discharge tube is connected to an evacuating pump, through a stopcock and tubes containing KOH. The apparatus is first evacuated, and the cupric chloride is heated by passing a current of 1·3 to 1·7 amps. through the electric furnace. The vapour is kept flowing, by continuously heating the tube and keeping the pump running and the discharge tube is excited by uncondensed transformer discharge. The colour of the discharge is greenish blue. The spectrum obtained is photographed on Hilger E_3 and Medium Quartz Spectrographs. Ilford ordinary plates and Kodak B 20 process regular plates are used.

The spectrum obtained in the present experiments with transformer discharge, is similar to that obtained by previous workers with high frequency discharge. In the visible region there are a large number of discrete bands, part of which have been analysed by Cameron and Elliot as due to Cl_2^+ molecule. In the ultra-violet region, there are a number of continuous bands. The wavelengths and wave-numbers of the maxima of continuous bands, as measured from a number of plates, are given in Table I. The

Table I

Set No.	Cameron and Elliot (High frequency discharge)	Singh and Adiga (High frequency discharge)	Present experiments (Transformer discharge)			
	λ	λ	Intensity	λ_{air}	λ_{vac}	$\Delta\nu$
I	3063	3063	8	3063	32638	
	2957	2954	3	2957	33808	(1170)
	2881	2880	4	2881	34700	(892)
	2819	2818	3	2820	35451	(751)
	2758	2759	2	2760	36221	(770)
	2714	2718	1	2715	36822	(601)
II	2564	2564	10	2565	38975	
	2432	2428	7	2430	41140	(2165)
		2349	5	2352	42504	(1364)
		2287	3	2287	43712	(1208)
		2200	2	2197	45502	(1790)
		2139	1	2145	46605	(1903)
		2076	?	2097	47672	(1067)
III		2001	2	1997*	50059	
		1918	1	1928*	51850	(1791)
		1865 ?	?	1855*	53890	(2040)

* These bands are overlapped by Schumann-Runge oxygen absorption bands.

intensities given are relative values visually estimated for the bands obtained on Ilford ordinary plates. The wavelengths of these continua as reported by previous workers, are also given in the table.

General Explanation of the Bands

The bands may apparently be divided into three sets. In bromine molecule there are three states $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u.1_u\,(^3\Sigma_u^+)$, $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2.1_g\,(^3\Pi_{1g})$; and $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2.1_g\,(^1\Pi_g)$ at 47000, 55534 and 66444 cm.$^{-1}$ which gives rise to groups of diffuse bands in the regions 4224–3260 Å, 3600–2688 Å and 2655–2400 Å respectively (Paper IV). By analogy with bromine we may take that the three sets of bands of Table I arise in the three states $1_u\,(^3\Sigma_u^+)$ $1_g\,(^3\Pi_{1g})$ and $1_g\,(^1\Pi_g)$ respectively. There is a fourth state $\Pi_{2,1/g}$ at 66400 cm.$^{-1}$ in bromine which gives rise to two groups of diffuse bands in extreme short-wave side. The corresponding bands in chlorine will probably lie in the vacuum ultra-violet region.

There are six continuous bands in the first set all of which, as said above, probably arise in the state $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u.1_u\,(^3\Sigma_u^+)$. They cannot, however, be explained as forming one sequence coming from different vibrational levels of the state $1_u\,(^3\Sigma_u^+)$ and having a flat potential energy curve for their final levels as the mutual wavenumber separations of the bands are so irregular and great that they cannot represent the vibrational frequencies of chlorine molecule. So these bands have to be explained as arising in the state $1_u\,(^3\Sigma_u^+)$ and having six different repulsive states for their final levels. These repulsive states must have *gerade* electronic terms as the initial state is an *ungerade* one. In a similar way, the continuous bands of the second set which arise in $1_g\,(^3\Pi_{1g})$ state, will have seven repulsive states for their final levels. These repulsive states will have *ungerade* electronic terms as the initial state is $1_g\ (^3\Pi_{1g})$ and as such they will be different from the repulsive states of the bands of the first set. There are only three continuous bands in the third set. Probably this set consists of some more bands in the vacuum region below 1850 Å. These three bands which probably arise in $1_g\,(^1\Pi_g)$ can be explained to have for their final levels three *ungerade* unstable states which are probably the same as those of the final levels of the first three bands of the first set.

Electronic Terms and Transitions Involved

Now we have to determine the electronic terms of the various repulsive states. From a combination of $^2P_{\frac{1}{2}} + {}^2P_{\frac{1}{2}}$ atoms we get 0_g^+, 1_u and 0_u^- of which only 0_g^+ can combine with $1_u\,(^3\Sigma_u^+)$. 0_g^+ is to be correlated with $(^1\Sigma_g^+)$ of case (*a*) type which arises from the configuration $\sigma_g^2, \pi_u^4, \pi_g^2, \sigma_u^2$. We can attribute the term $0_g^+\,(^1\Sigma_g^+)$ to the repulsive state of the first band

at 3063 Å of the first set. This seems to be justified because a corresponding band in bromine at 4224 Å is explained by a similar transition. From a combination of $^2P_{\frac{1}{2}} + {}^2P_{3/2}$ atoms we get the *gerade* terms 0_g^+, 1_g, 2_g, 1_g and 0_g^- all of which can combine with $1_u\,(^3\Sigma_u^+)$ according to selection rules for case (*c*) type coupling. Of these, $0^+{}_g$ and 1_g can be correlated with $^3\Sigma_g^-$, 2_g with $^1\Delta_g$, 1_g with $^1\Pi_g$ and 0_g^- with $^3\Pi_{0g}{}^-$ where $^3\Sigma_g^-$ and $^1\Delta_g$ arise from the configuration $\sigma_g{}^2, \pi_u{}^4, \pi_g{}^2, \sigma_u{}^2$ and $^1\Pi_g$ and $^3\Pi_{0g}{}^-$ have the configuration $\sigma_g{}^2, \pi_u{}^3, \pi_g{}^4, \sigma_u$. We can attribute the states $0_g^+\,(^3\Sigma_g^-)$, $1_g\,(^3\Sigma_g^-)$ $2_g\,(^1\Delta_g)$, $1_g\,(^1\Pi_g)$ and $0_g^-\,(^3\Pi_0{}^-{}_g)$ to the final levels of the five bands from second to sixth of the first set.

The transitions for the bands of the first set can be written as:*

1. Band at 3063 Å. $\sigma_g, \pi_u{}^4, \pi_g{}^4, \sigma_u.1_u\,(^3\Sigma_u^+) \rightarrow \sigma_g{}^2, \pi_u{}^4, \pi_g{}^2, \sigma_u{}^2.0_g^+(^1\Sigma_g^+)$
2. Band at 2957 Å ,, ,, → ,, $0_g^+\,(^3\Sigma^-{}_g)$
3. Band at 2881 Å ,, ,, → ,, $1_g\,(^3\Sigma^-{}_g)$
4. Band at 2820 Å ,, ,, → ,, $2_g\,(^1\Delta_g)$
5. Band at 2760 Å ,, ,, → $\sigma_g{}^2\,\pi_u{}^3, \pi_g{}^4, \sigma_u.1_g\,(^1\Pi_g)$
6. Band at 2715 Å ,, ,, → ,, $.0_g\,(^3\Pi_0{}^-{}_g)$

---

* In determining the electronic terms and transitions we have taken that the coupling here, as in the case of bromine and iodine, has a tendency towards (*c*) type coupling. If the coupling is strictly case (*a*) or (*b*) type, the second and the third transitions, *viz.*, from $1_u\,(^3\Sigma_u^+)$ to $0_g^+\,(^3\Sigma_g^-)$ and to $1_g\,(^3\Sigma_g^-)$ will not be possible because of $+ \rightarrow -$ prohibition rule. According to case (*a*) type coupling the electronic terms that are possible from $^2P + {}^2P$ atoms are[5] $^1\Sigma_g^+$, $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Pi_g$, $^3\Pi_{0g}{}^-$, $^3\Pi_{0g}{}^+$, $^3\Pi_{1g}$, $^3\Pi_{2g}$ and $^1\Sigma_g^+$ of which the last term $^1\Sigma_g^+$ corresponds to the ground state. Of the remaining the only terms that can combine with $1_u\,(^3\Sigma_u^+)$, taking that singlet $\leftrightarrow$ triplet prohibition rule is not strict, are $^1\Sigma_g^+$, $^1\Pi_g$, $^3\Pi_{o-g}$, $^3\Pi_{0g+}$, $^3\Pi_{1g}$ and $^3\Pi_{2g}$ which may be attributed to the final levels of the six bands of the first set. The electronic configuration of the term $^1\Sigma_g^+$ as well as of $^3\Sigma_g^-$ and $^1\Delta_g$ is $\sigma_g{}^2$, $\pi_u{}^4$, $\pi_g{}^2$, $\sigma_u{}^2$ and of $^1, {}^3\pi_g$ is $\sigma_g{}^2$, $\pi_g{}^3$, $\pi_u{}^4$, σ_u. The six transitions for the bands of the first set, if there is case (*a*) type coupling may be given as

1st band :	$\sigma_g, \pi_u{}^4, \pi_g{}^4, \sigma_u.$	$^3\Sigma_u^+$	→	$\sigma_g{}^2, \pi_u{}^4, \pi_g{}^2, \sigma_u{}^2.$	$^1\Sigma_g^+$
2nd band :	,,	,,	→	$\sigma_g{}^2, \pi_u{}^3, \pi_g{}^4, \sigma_u.$	$^1\Pi_g$
3rd band :	,,	,,	→	,,	$^3\Pi_0{}^-{}_g$
4th band :	,,	,,	→	,,	$^3\Pi_0{}^+{}_g$
5th band :	,,	,,	→	,,	$^3\Pi_{1g}$
6th band :	,,	,,	→	,,	$^3\Pi_{2g}$

Nine repulsive states are necessary in the case of bromine to explain the bands arising in $\sigma_g, \pi_u{}^4, \pi_g{}^4, \sigma_u, 1_u\,(^3\Sigma_u^+)$ and there are only six electronic terms according to case (*a*) type coupling which are, therefore, inadequate to explain all the repulsive states. On the other hand, there are just nine electronic terms according to case (*c*) type which can be attributed to the nine repulsive states to explain all the bands arising in $1_u\,(^3\Sigma_u^+)$ state. So in bromine it can be definitely said that the coupling is near case (*c*) type. But in chlorine we cannot say like that.

Now we turn to the second set which consists of seven continuous bands all of which as said above, will arise in the state $\sigma_g^1, \pi_u^4, \pi_g^3, \sigma_u^2$; $1_g\,(^3\Pi_{1u})$ and have for their final levels seven *ungerade* states. There are four ungerade states $\sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2$; $0_u^-\,(^1\Sigma_u^-)$; $\sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2$; $1_u\,(^3\Delta_{1u})$; $\sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2$; $2_u\,(^3\Delta_{2u})$; $\sigma_g^2, \pi_u^4, \pi_g^3, \sigma_u$; $1_u\,(^1\Pi_u)$ in bromine which dissociate into $^2P_{3/2} + {}^2P_{\frac{1}{2}}$ atoms which correspond to the final levels of groups of diffuse bands. Taking a similarity, we may attribute these terms to the final levels of the first four continuous bands of the second set. The final levels of the remaining three bands may be attributed to the three states $0_u^-(^3\Pi_{0u}^-)$, $1_u\,(^3\Pi_{1u})$ and $2_{\cdot u}\,(^3\Pi_{2u})$ which arise from the configuration $\sigma_g^2, \pi_u^4, \pi_g^3, \sigma_u$ and dissociate into two $^2P_{3/2}$ atoms. It may be mentioned that transitions from $1_g\,(^3\Pi_{1g})$ to $0_u^-(^3\Pi_{0^-u})$, $1_u\,(^3\Pi_{1u})$ and to $2_u\,(^3\Pi_{2u})$ are not, however, observed in iodine and bromine. The transitions for the seven continuous bands may be written as:

1. λ 2565: $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2.1_g\,(^3\Pi_{1g}) \rightarrow \sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2.0_u^-(^1\Sigma_u^-)$
2. λ 2430: ,, ,, → ,, $.1_u\,(^3\Delta_{1u})$
3. λ 2352: ,, ,, → ,, $.2_u\,(^3\Delta_{2u})$
4. λ 2287: ,, ,, → $\sigma_g^2, \pi_u^4, \pi_g^3, \sigma_u\,.1_u\,(^1\Pi_u)$
5. λ 2197: ,, ,, → ,, $.0_u^-\,(^3\Pi_{0u}\text{-})$
6. λ 2145: ,, ,, → ,, $.1_u\,(^3\Pi_{1u})$
7. λ 2097: ,, ,, → ,, $.2_u\,(^3\Pi_{2u})$

All these seven transitions are possible according to selection rules for case (*c*) type and case (*a*) type, taking of course that the prohibition rule singlet $\longleftrightarrow$ triplet is not strict.

The three bands of the third set are said to be arising in the state $\sigma_g, \pi_u^4, \pi_g^3, \pi_u^2$, $1_g\,(^1\Pi_g)$, and having for their final levels three *ungerade* repulsive states which are the same as those of the first three bands of the second set. The transitions can be written as

1. λ 1997: $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2.1_g\,(^1\Pi_g) \rightarrow \sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2.0_u^-(^1\Sigma_u^-)$
2. λ 1928: ,, ,, → ,, $.1_u\,(^3\Delta_{1u})$
3. λ 1855: ,, ,, → ,, $.2_u\,(^3\Delta_{2u})$

Location of the Initial Level

The position of the three stable states $1_u\,(^3\Sigma_u^+)$; $1_g\,(^3\Pi_{1g})$ and $1_g\,(^1\Pi_g)$ are now to be calculated. In the case of iodine and bromine the repulsive curves are nearly flat (curves of bromine will be steep compared to those of iodine), and the dissociation energies of $^2P_{\frac{1}{2}} + {}^2P_{\frac{1}{2}}$, $^2P_{3/2} + {}^2P_{\frac{1}{2}}$; and $^2P_{3/2} + {}^2P_{3/2}$ atoms are known; so, the position of these states could be

calculated to a fairly good approximation. The repulsive curves in chlorine are steep and so it will be more difficult to calculate the positions of the stable states. However, we can calculate the minimum values (lower limits) for the positions as follows. The last band of the first set dissociates into $^2P_{\frac{1}{2}} + {}^2P_{3/2}$ atoms at 20903 cm.$^{-1}$* As the maximum of this continuous band is at 36822 cm.$^{-1}$ and as the repulsive curve is steep, the minimum position of the initial state $1_u\,(^3\Sigma_u^+)$ will be at 36822+20903 = 57725 ~ 58000 cm.$^{-1}$ The last band of the second set, *viz.*, the band at 47672 cm.$^{-1}$ dissociates into two $^2P_{3/2}$ atoms at 20022 cm^{-1}. The minimum value for the position of the state $1_g\,(^3\Pi_{1g})$ which is the initial state of all the bands of the second set is 20022+ 47672= 67694 ~ 67700 cm.$^{-1}$ Similarly as the last band of the third set, *viz.*, the band at 53890 cm.$^{-1}$ dissociates into $^2P_{\frac{1}{2}} + {}^2P_{3/2}$ atoms at 20903 cm.$^{-1}$, the minimum value for the position of the state $1_g\,(^1\Pi_g)$, which is the initial state of the bands of the third set, is at 20903+ 53890 = 74793 ~ 75000 cm^{-1}. We can take that the minimum values thus calculated, represent the approximate values for the positions of the states $1_u\,(^3\Sigma_u^+)$, $1_g\,(^3\Pi_{1g})$ and $1_g\,(^1\Pi_g)$.

Some Remarks on the Absorption Spectrum of Chlorine

Of the seven repulsive states $0_u^-(^1\Sigma_u^-)$, $1_u\,(^3\Delta_{1u})$, $2_u\,(^3\Delta_{2u})$, $1_u\,(^1\Pi_u)$, $0_u^-\,(^3\Pi_{\sigma u})$, $1_u\,(^3\Pi_{1u})$ and $2_u\,(^3\Pi_{2u})$ which respectively form the final levels of the seven bands of the second set, only $1_u\,(^3\Delta_{1u})$, $1_u\,(^1\Pi_u)$ and $1_u\,(^3\Pi_{1u})$ can combine with the ground state $0_g^+\,(^1\Sigma_g^+)$ according to case (*c*) type selection rules. And according to selection rules for case (*a*) type, only $1_u\,(^1\Pi_u)$ can combine with $0_g^+\,(^1\Sigma_g^+)$. $1_u\,(^3\Pi_{1u})$ may also combine with $0_g^+\,(^1\Sigma_g^+)$ if the coupling is not strictly case (*a*) type. In absorption there are discrete bands between 5760—4800 Å, which are due to transition from the ground state to final level $0^+{}_u\ (^3\Pi_{0u}{}^+)$. These discrete bands are followed by a continuous absorption which extends into the ultra-violet and which has a strong maximum at 30300 cm.$^{-1}$ This strong maximum is probably due to the transition from the ground state to the repulsive state $1_u\,(^1\Pi_u)$. Aickin and Bayliss[9] indicate the probable presence of an extremely weak maximum at about 23550 cm.$^{-1}$ This may be due to the transition from the ground state to the repulsive state $1_u\,(^3\Pi_{1u})$.

Besides the continuous absorption already stated, Cordes and Sponer[8] have reported continuous absorption in the vacuum region, with a probable

* The accepted value for the dissociation energy of the ground state of the chlorine molecule[6] is 2·47 volts or 20022 cm.$^-$ which represents dissociation into two normal atoms. The energy difference[7] Cl $(^2P_{3/2})$–Cl $(^2P_{1/2})$ is 881 cm.$^{-1}$ So the energy of dissociation of chlorine molecule built up of $(^2P_{3/2} + {}^2P_{1/2})$ chlorine atoms is 20903 and that of $^2P_{1/2} + {}^2P_{1/2}$ chlorine atoms is 21784 cm.^{1}

maximum at 1560 Å (60000 cm.$^{-1}$). The long wave limit of this continuum changes with pressure and at a pressure of 1·2 atmospheres, it reaches 1900 Å after which it is not affected by further increase of pressure. The corresponding continuum in bromine which has a maximum at about 2250 Å is explained as due to a transition from the ground state to a steep repulsive curve $\sigma_g^2, \pi_u^3, \pi_g^3, \sigma_u^2.1_u\,(^3\Sigma_u^+)$ which dissociates into two $^2P_{\frac{1}{2}}$ atoms. A similar transition will explain the extensive continuum in the vacuum region in chlorine.

The Potential Energy Diagram for Cl_2

Now we turn our attention to the potential energy diagram. The potential energy curves for the states $0_g^+\,(^1\Sigma_g^+)$ and $0_u^+\,(^3\Pi_{0^+u})$ are drawn by using Morse equation, and known constants.[6] (In iodine and bromine the vibrational frequencies for the states that give rise to groups of diffuse bands are known and so r_e values for these states could be calculated approximately by using Badger's formula. In chlorine, as the vibrational frequencies of the stable states $1_u\,(^3\Sigma_u^+)$, $1_g\,(^3\Pi_{1g})$ and $1_g\,(^1\Pi_g)$ are not known,

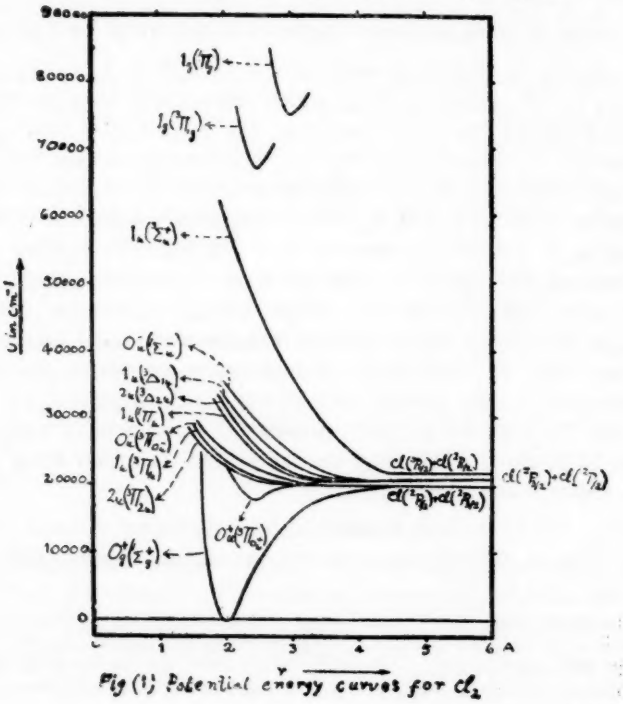


Fig (1) Potential energy curves for Cl_2

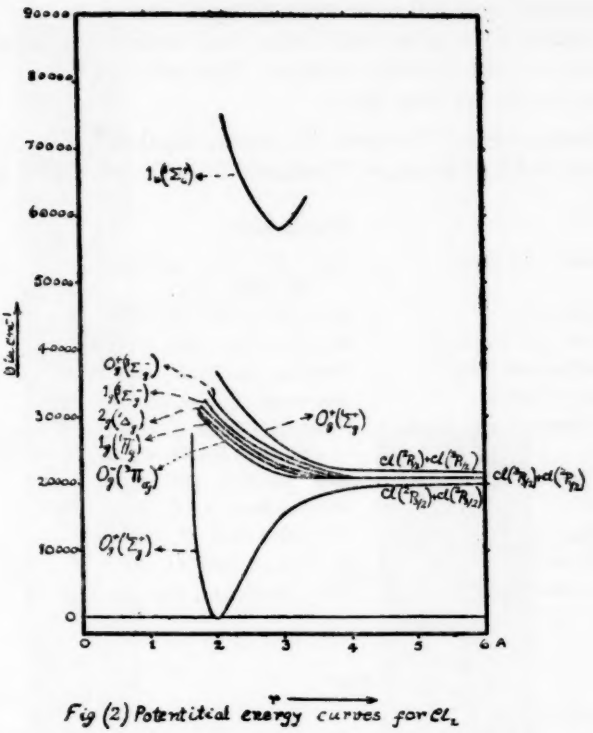


Fig (2) Potentitical energy curves for Cl_2

their r_e values cannot be calculated. The rough positions of the levels $1_u(^3\Sigma_u^+)$, $1_g(^3\Pi_{1g})$, $1_g(^1\Pi_g)$ are indicated. The repulsive curves are also drawn, as in the case of iodine and bromine. The curves for the unstable *gerade* states are shown separately in Fig. 2, for the sake of clarity.

Summary

Wavelengths of the maxima of continuous bands of chlorine in the ultra-violet obtained with uncondensed transformer discharge, are given. These are practically the same as were previously recorded by other observers. The chlorine spectrum is shown to be apparently similar to that of iodine and bromine. The bands are conveniently arranged in three sets which are shown to be respectively arising in the three states $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u . 1_u(^3\Sigma_u^+)$; $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2 . 1(^3\Pi_{1g})$; $\sigma_g, \pi_u^4, \pi_g^3, \sigma_u^2 . 1_g(^1\Pi_g)$. The approximate positions are at about 58000, 67700 and 75000 cm.$^{-1}$ respectively whereas for bromine they are at 47000, 55534 and 61444 cm.$^{-1}$ and for iodine they are at 44900, 51528 and 58572 cm.$^{-1}$ The final states of all these bands

will be repulsive, and will have steep potential energy curves. They have been attributed, in analogy with iodine and bromine, to those electronic states which are theoretically possible. The potential energy diagram for chlorine molecule has been given.

The author wishes to express his sincere thanks to Prof. R. K. Asundi for guidance and to Kamalapat Singhania Trust for the award of a scholarship.

References

1. Cameron and Elliot .. *Proc. Roy. Soc.*, 1937, **158A**, 681; 1938, **164A**, 53; 1939, **169A**, 463.
2. (*a*) Augerer, V. .. *Zs. f. Phys.* 1922, **11**, 167.
   (*b*) Strutt and Fowler .. *Proc. Roy. Soc.*, 86A, 105, 1911.
   (*c*) Ludlam and West .. *Proc. Roy. Soc. Edin.*, 1923–24, **44**, 185.
3. Singh and Adiga .. *Science and Culture*, 1944–45, **10**, 95.
4. Venkateswarlu .. "Emission Bands of Halogens," Parts I to IV, *Proc. Ind. Acad. Sci.* **24**, 480; **25**, 119 to 150.
5. Mulliken .. *Rev. Mod. Phys.*, 1932, **4**, 70.
6. Sponer .. *Molekul–Spectrum*, **1**, (Berlin), 1935.
7. Turner .. *Phys. Rev.*, 1926, **27**, 397.
8. Cordes and Sponer .. *Zs. f. Phys.*, 1930, **63**, 334.
9. Aickin and Bayliss .. *Trans. Farad. Soc.*, 1937, **33**, 1333.

The Spectra marked a (1, 2) are taken on a Medium Hilger Quartz Spectrograph on Ilford Ordinary Plates.
The Spectra marked b (1, 2, 3) are taken on E_3 Hilger Quartz Spectrograph on Ilford Ordinary Plates.
Wavelengths of the continuous bands are marked.

MAXIMAL-HAUSDORFF SPACES

By A. Ramanathan

(Department of Mathematics, University of Madras)

Received January, 1947

(Communicated by Dr. R. Vaidyanathaswamy, M.A., Ph.D., D.Sc.)

§1. Introduction

§1. 1. Bicompact spaces form a very important class of topological spaces; the principal properties relating to them will be found in Alexandroff and Hopf, *Topologie*, Kap. II. Among the bicompact spaces, the Hausdorff bicompact spaces occupy, as is well known, a special position; their characteristic property has been stated in the following form by Dr. R. Vaidyanathaswamy in his *Treatise on Set Topology*, p. 104 (in the press):

A Hausdorff bicompact space is both minimal-bicompact and maximal-Hausdorff.

The Author further adds:

It is not known whether there exist topologies on an infinite set R which are minimal-bicompact without being Hausdorff or maximal-Hausdorff without being bicompact.

The purpose of the present paper is to supply a partial answer to this question by proving that a maximal-Hausdorff space need not necessarily be bicompact.

The first important result obtained is that a maximal-Hausdorff space is necessarily H-closed. That the only regular maximal-Hausdorff spaces are the Hausdorff bicompact spaces follows from a well-known theorem of Alexandroff and Hopf, namely that a H-closed regular space is bicompact. A method of strengthening a Hausdorff space at an irregular point is shown in Theorem IV, which leads to some negative results. In this connection it is remarkable that a space constructed by Urysohn for a different purpose happens to be maximal-Hausdorff without being bicompact. This is proved by the necessary and sufficient condition enunciated and proved for a Hausdorff space to be maximal-Hausdorff, namely that every neighbourhood of every point of the space should contain an open domain neighbourhood of the point whose complement is H-closed.

I am under a permanent debt of gratitude to Dr. R. Vaidyanathaswamy, Reader in Mathematics, University of Madras, for having indefatigably

helped me during the arduous discussions I have had with him on the subject and particularly in the enunciation and proof of the last mentioned theorem.

§1. 2. Strength of Topologies.

We are concerned only with topological spaces R of any sort of elements defined by neighbourhood systems satisfying the well-known postulates of Hausdorff, *viz.*,

$\mathbf{H_1}$. *Each point of R has at least one neighbourhood and is contained in every one of its neighbourhoods.*

$\mathbf{H_2}$. *If $U(p)$, $V(p)$ are any two neighbourhoods of p then there exists a neighbourhood of p which is contained in $U(p) \,.\, V(p)$.*

$\mathbf{H_3}$. *To each neighbourhood $U(p)$ of p there exists a neighbourhood $V(p)$ of p such that $U(p)$ contains a neighbourhood of each point of $V(p)$.* It is well known that any neighbourhood system satisfying H_1, H_2, H_3 introduced in the set R defines uniquely a topological structure in R. In this structure

(i) for any set $X \subset R$ we have $\bar{X}$ is the set of points of R every neighbourhood of each of which has non-null intersection with X;

(ii) a set is open if it contains a neighbourhood of each of its points;

(iii) any point is an interior point of every one of its neighbourhoods.

Let there be two neighbourhood systems the U-system and the V-system introduced in R, both of course satisfying H_1, H_2, H_3. The two systems are said to be *equivalent* if and only if they define the same topological structure in R. The necessary and sufficient condition for this is that *for each point p of R, every $U(p)$ contains a $V(p)$ and every $V(p)$ contains a $U(p)$.*

The totality of open sets of a topological space R, when each of them is considered as a neighbourhood of each of its points, form a neighbourhood system of the space equivalent to the given neighbourhood system and will be conveniently used to replace the given system.

A topological space R is said to be (*a*) a T_1-space if every point $p \epsilon R$ has a neighbourhood not containing any other assigned point q; (*b*) a T_2- or *Hausdorff space* if every pair of distinct points are *H-separable*, *i.e.*, have disjoint neighbourhoods; (*c*) a *Urysohn space* if every pair of distinct points are *U*-separable, *i.e.*, have neighbourhoods whose closures are disjoint. Two distinct points of R are said to be *U-inseparable* if they possess no neighbourhoods whose closures are disjoint. A point p of R is said to be *regular* if every neighbourhood of the point contains the closure of another neighbourhood of the point; the space itself is called regular if every point

of the space is regular. An irregular point of R is called, after M. H. Stone, *semi-regular* if every neighbourhood of the point contains the interior of the closure of another neighbourhood of the point. It is obvious that every Urysohn space is a Hausdorff space and that every regular space is a Urysohn space; whereas, not all Urysohn spaces are regular spaces.

Let there be two systems of neighbourhoods the U-system and the V-system introduced in a set R both satisfying H_1, H_2, H_3. (i) We say, after Dr. R. Vaidyanathaswamy, that the V-system is *stronger* than the U-system at a point $p \epsilon R$, if every $V(p)$ contains a $U(p)$ and if there is at least one $U(p)$ which contains no $V(p)$. Suppose two different topological structures f, ϕ are defined in a set R. Let us denote by $(R; f)$ the topological space R whose topological structure is f. (ii) The topology ϕ is said to be *stronger* than f, if every open set of $(R; \phi)$ is also an open set of $(R; f)$ and if there is at least one open set of $(R; f)$ which is not open in $(R; \phi)$. (iii) A Hausdorff space $(R; f)$ is said to be *maximal-Hausdorff* if any topology on R which is stronger than f renders the space non-Hausdorff.

Let the U-system and the V-system define respectively the topological structures f and ϕ in a set R. We may suppose that $\{U\}$ and $\{V\}$ represent the absolute neighbourhood systems of the topologies f and ϕ respectively. Then we have

Theorem I.

If ϕ is stronger than f, then there is at least one point at which the V-system of neighbourhoods is stronger than the U-system.

Since ϕ is stronger than f, there is at least one set A which is open in f but not open in ϕ. Let p be a boundary point of A in ϕ-topology. Now any neighbourhood $V(p)$ of p in ϕ is open in ϕ, therefore also open in f and hence is a $U(p)$. But since A is open in f there is a $U(p)$, say $U_0(p)$, which is contained in A. Since p is a boundary point of A in ϕ there is no $V(p)$ which is contained in A. Hence $U_0(p)$ contains no $V(p)$. So $\{V\}$ is stronger than $\{U\}$ at the point p.

Theorem II.

If ϕ is stronger than f, then there exists a topology ψ which is equivalent to ϕ at just one point $p \epsilon R$ and equivalent to f at all other points of R (it being assumed that f is a T_1-topology).

For, there is a set G which is open in f but not open in ϕ and hence it has a boundary point p in ϕ. Take the ϕ-neighbourhoods for the point p and the f-neighbourhoods for all other points of R. The system of

neighbourhoods thus defined satisfy evidently H_1, H_2. To show that it satisfies also H_3, let us observe that a $\phi(p)$ contains a ϕ-neighbourhood of every one of its points. But a ϕ-neighbourhood of any point other than p is also a f-neighbourhood of that point. Hence any $\psi(p)$ contains a ψ-neighbourhood of every one of its points. Thus H_3 is satisfied by $\{\psi(p)\}$. If q is any point other than p, then the neighbourhoods of q which are disjoint with p by themselves form a system of neighbourhoods of the point equivalent to the given system, since the topology f is T_1. We see immediately that the ψ-system for points other than p also satisfies H_3. The topology defined by the new system of neighbourhoods satisfies the conditions of the theorem.

Corollary.

It follows from this theorem that, in order to show that the Hausdorff space $(R; f)$ is maximal-Hausdorff, it is sufficient to show that the neighbourhood system of the space cannot be strengthened at any point without destroying the Hausdorff character of the space. For, if there exists a Hausdorff topology ϕ stronger than f, then there would exist a topology ψ which is equivalent to f at all points except at a single point at which it is equivalent to ϕ. Then ψ will also be Hausdorff and would be obtained from f by strengthening at a single point.

§2. Regular Maximal-Hausdorff Spaces

§2·1. H-closed spaces.

We say that a topological space R can be *topologically imbedded* in another topological space S if R is homeomorphic to a subset of S. We say that a Hausdorff space R is *H-closed* if it is closed in every Hausdorff space in which it can be topologically imbedded. It is obvious that a finite set of R is always H-closed; the set $(1, 2, 3, \ldots)$ of the real number space is not H-closed. Alexandroff and Hopf (*loc. cit.*, p. 90) have proved

§2·2. *A necessary and sufficient condition for a Hausdorff space R to be H-closed is that from every open covering $\{G\}$ of R, it should be possible to select a finite number of elements $G_1, G_2, \ldots G_n$ say, such that*

$$\sum_1^n \bar{G}_i = R.$$

§2·3. Theorem III

A Maximal-Hausdorff space is necessarily H-closed.

If the Hausdorff space R is not H-closed then we shall show that its topology can be strengthened at any point p, without derogation to the Hausdorff character of the space. Now by §2.2 there exists an open covering $\{G\}$ of R such that for every choice of the finitely-many elements

$G_1, G_2, \ldots . G_n$ of $\{G\}$ the open set $F = (R - \sum_1^n G_i)$ is non-null. Now the family of open sets F are such that the intersection of any two F's is a F. Moreover, if we choose for a neigbourhood $U(p)$ of any point p, an element of $\{G\}$ which contains p then $U(p)$ is disjoint with $\{R - \overline{U(p)}\}$ which by definition is a F. Hence there is at least one F which is disjoint with a $U(p)$. Since the intersection of any two F's is non-null it follows that if a $U(p)$ is disjoint with a F then that $U(p)$ can contain no F. Let us now define a system of neighbourhoods $\{V(p)\}$ for p where the $V(p)$'s are sets of the form $\{U(p) + \text{a set } F\}$. Now the $V(p)$'s are open sets of the space R which contain p. Since the intersection of any two $U(p)$'s is a $U(p)$ and the intersection of any two F's is a F, it follows that the intersection of any two $V(p)$'s is a $V(p)$. Further there is at least one $U(p)$ which contains no $V(p)$. Hence the system $\{V(p)\}$ is stronger than the system $\{U(p)\}$. Let now q be any point of R other than p. Then there exists a $U(p)$ disjoint with a $U(q)$ and there exists a F disjoint with a $U(q)$. Hence there exists a $V(p)$ disjoint with a $U(q)$. Thus the V-topology is a Hausdorff topology which is stronger than the U-topology. Hence the U-topology is not maximal-Hausdorff. Q.E.D.

§2·4. The condition of Theorem III is not sufficient. The following example of Alexandroff and Hopf (*loc. cit.*, p. 31), constructed for a different purpose, exhibits a H-closed space which is not maximal-Hausdorff.

Example 1.—Let R be the unit length $0 \leqslant p \leqslant 1$ of the Arithmetical continuum, D the set of all points $1/n$, $n = 1, 2, 3, \ldots .$ If $0 < p < 1$, then let $J(p)$ be an arbitrary open interval of R which contains p; if $p = 0$ or 1, let $J(p)$ be a half-interval $0 \leqslant t < a$ or $a < t \leqslant 1$ respectively, where a lies between 0 and 1 and is otherwise arbitrary. When $p \neq 0$, let $J(p)$ be a neighbourhood of p. Let the sets of the form $\{J(0) - D\}$ be the neighbourhoods of the point 0.

The space R thus constructed is a Hausdorff space in which 0 is an irregular point. It is H-closed. For, consider any open covering $\{G\}$ of R. Evidently the G's may be open intervals of the form $J(p)$ if they do not contain 0 and of the form $\{J(0) - D\}$ if they contain 0. We see that $\overline{G(0)}$ is always an open interval of the form $J(0)$. The subspace $\{R - \overline{G(0)}\}$ can always be covered by the closures of a finite number of G's. Hence R itself can be covered by the closures of a finite number of G's.

Evidently the given neighbourhood system is weaker at the point 0 than, and equivalent at all other points to, the neighbourhood system of the space R under its usual topology where the neighbourhoods of the

point 0 are the half-open intervals $J(0)$. The usual topology of R is a Hausdorff topology and hence the given topology of R is not maximal-Hausdorff. Q.E.D.

§2·5. Corollary

The only regular maximal-Hausdorff spaces are the Hausdorff bicompact spaces.

This follows from Theorem III and the following theorem due to Alexandroff and Hopf (*loc. cit.*, p. 91) *viz.*,

A H-closed regular space is bicompact.

§ 3. Irregular Maximal-Hausdorff Spaces

§3·1. The following method of strengthening a Hausdorff space at an irregular point is often useful.

Theorem IV

The topology of a Hausdorff irregular space can be strengthened at any irregular point p by choosing the regular neighbourhoods of p as its new neighbourhoods; the strengthened topology is necessarily T_1 and would be Hausdorff if p is U-separable from every other point of the space.

The intersection of two regular neighbourhoods of p is evidently a regular neighbourhood of p. Since we are not altering the neighbourhoods at other points, it follows that the regular neighbourhoods of p satisfy H_1, H_2, H_3 and can be taken as new neighbourhood system at p.

Let q be any other point and $U(p)$, $U(q)$ disjoint neighbourhoods of p, q (which exist as the space is Hausdorff); as $(R-q) \supset \overline{U(p)}$, it follows that $(R-q)$ is a regular neighbourhood of p disjoint with q. Thus the strengthened topology is T_1. If every point q other than p is U-separable from q, there are neighbourhoods $U(p)$, $U(q)$ of p and q such that $\overline{U(p)} \cdot \overline{U(q)} = 0$. Hence Ext. $U(q)$, which contains $\overline{U(p)}$ is a regular neighbourhood of p disjoint with the neighbourhood $U(q)$ of q. Thus p, q are H-separable in the strengthened topology.

§3·2. Corollary I

A Hausdorff space with only one irregular point cannot be maximal-Hausdorff.

If p be the only irregular point of a Hausdorff space R, then p is U-separable from every other point of R. For, if r be any point of R other than p, then there exist neighbourhoods $U(p)$, $U(r)$ such that $0 = U(p) \cdot U(r) = \overline{U(p)} \cdot U(r)$. But r is a regular point of R. Hence

there exists a neighbourhood $U_1(r)$ of r whose closure is contained in $U(r)$. It follows that $\overline{U(p)} \cdot \overline{U_1(r)} = 0$, *i.e.*, p and r are U-separable. The given space can be strengthened as explained in Theorem IV and the strengthened topology is Hausdorff by the same Theorem.

Example 1 given above, illustrates the present corollary. As further illustration we may consider the following space constructed by Dr. R. Vaidyanathaswamy (*loc. cit.*, p. 99) for a different purpose; the space is regular except at the point O, which is semi-regular.

Example 2.—Take the Cartesian plane with the rectangular axes $X'OX$, $Y'OY$. Consider the semi-circles $POP'S$ lying to the right of Y-axis. Define the neighbourhoods of O to be the union of O with the open semi-circles POP's. The neighbourhoods of the other points are the usual ones. The space thus constructed is a Hausdorff space for which, as can be easily seen, O is a semi-regular point. Replacing the given neighbourhoods of O by its usual ones, which form a stronger system than the given system, the space still remains Hausdorff. Hence the given space is not maximal-Hausdorff.

§3·3. Corollary II

If, in a Hausdorff irregular space, there exists at least one irregular point which is U-separable from every other point of the space, then the space cannot be maximal-Hausdorff.

For, if p be an irregular point of the Hausdorff space R, which is U-separable from every other point of the space, on replacing the given neighbourhood system at p by the system of regular neighbourhoods of p, we see, by Theorem IV, that p is H-separable from every other point of R and so R is Hausdorff in the strengthened topology. Hence the given space is not maximal-Hausdorff. Q.E.D.

§3·4. Corollary III

If every pair of distinct irregular points of a Hausdorff space are U-separable, then the space cannot be maximal-Hausdorff.

This is only a case with much stronger hypothesis than Corollary II. As an illustration of the present Corollary, let us consider the following example.

Example 3.—The set R of real numbers is topologised by ascribing to each number x as its neighbourhoods, the sets $(I_x - S)$ if x is irrational and the sets $\{x + (I_x - S)\}$ if x is rational, where I_x is any open interval containing x and S is the set of rational numbers.

The space thus defined is a Hausdorff space in which every point is irregular. Any pair of distinct points, however, are U-separable. The space, therefore, by Corollary III, is not maximal-Hausdorff and this may also be verified by the fact that the given neighbourhood system is weaker at every point than the neighbourhood system of the usual topology of the real number space which is a Hausdorff topology.

§3.5. An open set g of a topological space is an *open domain* of the space if and only if it satisfies any one of the following equivalent conditions: (i) g is the exterior of some open set; (ii) g is the exterior of its own exterior; (iii) g is the interior of its closure; (iv) g is the interior of some closed set. For fuller information *vide* Dr. R. Vaidyanathaswamy, *loc. cit.*, p. 91. A family of open sets $\{G\}$ of a topological space is called, after Dr. R. Vaidyanathaswamy, a *proximate covering* of the space if it covers the whole of the space with the possible exception of a *non-dense* set. It follows that the union of all sets of a proximate open covering is a *dense open* set.

3·6. Theorem V

A maximal-Hausdorff space is necessarily semiregular.

Any two distinct points p, q of the Hausdorff space have neighbourhoods $U(p)$, $U(q)$ such that $0 = U(p).U(q) = \overline{U(p)}.U(q) = U(p).\overline{U(q)}$. Hence $Int\ \overline{U(p)}$ is disjoint with $U(q)$ and similarly $Int\ \overline{U(q)}$ is disjoint with $U(p)$. Now if $U_1(p)$, $U_2(p)$ be any two neighbourhoods of p, then $\overline{U_1(p)}.\overline{U_2(p)} \supset \overline{U_1(p).U_2(p)}$ *so that* $Int\ \overline{U_1(p)}.Int\ \overline{U_2(p)} \supset Int\ \overline{U_1(p).U_2(p)}$. It follows that the system of open domains $\{Int\ \overline{U(p)}\}$ satisfy H_1, H_2, H_3 and if these be taken to form a new system of neighbourhoods for p then the system $Int\ \{\overline{U(p)}\}$ will be stronger than the system $\{U(p)\}$ if the point p is not semiregular. Hence if a Hausdorff space R contains at least one irregular point which is not semiregular then the topology of the space can be strengthened by replacing its neighbourhoods by the system of open domains containing the point as its new neighbourhoods without destroying the Hausdorff character of the space and so the given space would not be maximal-Hausdorff. If in the above argument the point p is a semiregular point so that its neighbourhoods are already open domains then $\{Int\ \overline{U(p)}\}$ will be equivalent to $\{U(p)\}$. We see therefore that, in order that a Hausdorff irregular space may be maximal-Hausdorff, the space should necessarily be semiregular. Q.E.D.

§3.7. We are now in a position to prove the necessary and sufficient condition for a Hausdorff space to be maximal-Hausdorff.

Theorem VI

The necessary and sufficient condition for a Hausdorff semiregular space R to be maximal-Hausdorff is that every neighbourhood of every point of the space should contain an open domain neighbourhood of the point whose complement is H-closed.

The condition is necessary.

For, suppose the condition is not satisfied. Then there exists a point p such that it has a neighhourhood $U_0(p)$* which contains no open domain-neighbourhood whose complement is H-closed. We shall prove that the topology can be strengthened at the point p without destroying the Hausdorff character of the space. In the first place, $(R-p)$ cannot be H-closed, for, if it were H-closed p would be an isolated point and would therefore be an open domain-neighbourhood contained in every neighbourhood of p contrary to hypothesis. We will now find an open covering of $(R-p)$ which contains no finite proximate covering of $(R-p)$. Now by hypothesis, $[S = R - U_0(p)]$ is not H-closed. Hence there is a covering of S by relative open sets $\{g_\alpha\}$ which contains no finite proximate covering of S. Let G_α be an open set of R such that $G_\alpha . S = g_\alpha$. Now for any point $q \epsilon S$ there is a $U(q) \subset g_\alpha$ and disjoint with a neighbourhood of p. This is possible since R is Hausdorff. For any point $r \epsilon U_0(p)$ choose an open set $U(r) \subset U_0(p)$ which is disjoint with a neighbourhood of p, which is again possible since R is Hausdorff. Consider the covering of $(R-p)$ constituted by the family of open sets consisting of the $U(q)$'s and the $U(r)$'s. No finite number of $\overline{U(q)}$'s can cover S for, otherwise the corresponding g_α's would constitute a finite proximate covering of S. But $S - \sum_1^m \overline{U(q)}$ is a relative open domain of S and therefore will have an interior. This interior can never be covered by any finite number of $\overline{U(r)}$'s since every $\overline{U(r)} \subset \overline{U(p)}$. Hence $F = (R-p) - \sum_1^m \overline{U(q)} - \sum_1^n \overline{U(r)}$ is never null; since each $U(q)$ and $U(r)$ is disjoint with a $U(p)$, a finite number of $U(q)$'s and $U(r)$'s are always disjoint with a $U(p)$, it follows that every F contains an open set containing p. Evidently the intersection of two F's is a F. Further $U_0(p)$ contains no F, for otherwise the closures of a finite number of $U(q)$'s and $U(r)$'s would cover S. Now the open sets $(p+F)$ satisfy the conditions for being taken for a new system of neighbourhoods for p. As each $p+F$ contains a $U(p)$ we see that $p+F$ is

* We may assume, without loss of generality, that $U_0(p)$ is an open domain neighbourhood of p.

stronger than or equivalent to the original system of neighbourhoods of p. But it is not equivalent to the original system since $U_0(p)$ contains no $p+F$. Hence the new system of neighbourhoods of p is stronger than the original system and so the V-topology is stronger than the given topology of R. Further the point p is H-separable from every point of the space under its new neighbourhood system for from the formation of the F's it is clear that there is a F disjoint with a $U(q)$ for any point $q \epsilon S$ and also a F disjoint with a $U(r)$ for any point $r \epsilon U_0(p)$. Hence the strengthened topology is Hausdorff and the given topology of R is not maximal-Hausdorff. Q.E.D.

The condition is sufficient. Suppose there exists a system $\{V(p)\}$ for a point p which is stronger than $\{U(p)\}$ so that there is a $U(p)$, say $U_0(p)$, which contains no $V(p)$. Then p would be a boundary point of $U_0(p)$ in the V-topology *i.e.*, a contact point of $[R - U_0(p)]$. But $[R - U_0(p)]$ is H-closed. Hence $[R - U_0(p)] + p$ cannot be a Hausdorff space; so that in the V-topology, p fails to satisfy the H-separability axiom with points in $\{R - U_0(p)\}$. Q.E.D.

The theorem is evidently verified in the case of Hausdorff bicompact spaces, where, as is well known, every closed subset is H-closed.

We now proceed to illustrate the theorem by consideration of a Hausdorff space constructed by Urysohn for a different purpose (*vide* Urysohn, Über die Mächtigkeit zusammenhängender Mengen; *Mathematische Annalen*, Band **94**, p. 268).

Example 4.—Let the space R be defined as follows:

$$R = a + b + \{a_{ij}\} + \{b_{ij}\} + c_i \ldots . (i, j = 1, 2, \ldots .)$$

A point of R shall be said to be of 0th, 1st or 2nd order according as the letter which represents the point contains no element, only one element or two elements respectively in the suffix.

The neighbourhoods are defined as follows:

$$U(a_{ij}) = a_{ij}; \quad U(b_{ij}) = b_{ij};$$

(*i.e., the points of the second order are isolated points.*)

$$\left.\begin{aligned} U^n(c_i) &= c_i + \sum_{j=n}^{\infty} (a_{ij} + b_{ij}) \\ U^n(a) &= a + \sum_{j=1}^{\infty} \sum_{i=n}^{\infty} a_{ij} \\ U^n(b) &= b + \sum_{j=1}^{\infty} \sum_{i=n}^{\infty} b_{ij} \end{aligned}\right\} n = 1, 2, 3 \ldots$$

The neighbourhoods satisfy H_1, H_2, H_3.

H_1: evident.

H_2: follows from the fact that for every point x

$$U^n(x).U^{n+h}(x) = U^{n+h}(x)$$

H_3: follows from the fact that only the points of the second order—which are in fact identical with their neighbourhoods—can be contained in a neighbourhood of any other point.

H-separability: is evidently satisfied for any two points of the same order; that it is satisfied for all other points also is seen from the following equalities:

1. (*a point of the second order and a point of the first order*):

$$U(a_{pq}).U^{q+1}(c_i) = 0,\ U(b_{pq}).U^{q+1}(c_i) = 0;$$

2. (*second order and 0th order*):

$$U(a_{pq}).U^{p+1}(a) = 0,\ U(b_{pq}).U^{p+1}(b) = 0;$$

$$U(a_{pq}).U^1(b) = 0,\ U(b_{pq}).U^1(a) = 0;$$

3. (*first order and 0th order*):

$$U^1(c_p).U^{p+1}(a) = 0,\ U^1(c_p).U^{p+1}(b) = 0.$$

However for arbitrary n and m,

$$\overline{U^n(a)}.\overline{U^m(b)} \supset \overline{U^{n+m}(a)}.\overline{U^{n+m}(b)}$$

$$\supset \overline{\left(\sum_{j=1}^{\infty}\sum_{i=n+m}^{\infty} a_{ij}\right)}\cdot\overline{\left(\sum_{j=1}^{\infty}\sum_{i=n+m}^{\infty} b_{ij}\right)}$$

$$\supset \overline{\left(\sum_{j=1}^{\infty} a_{(n+m)j}\right)}\cdot\overline{\left(\sum_{j=1}^{\infty} b_{(n+m)j}\right)}$$

$$\supset c_{n+m}.$$

Thus, in the space R, the points a and b are U-inseparable and consequently they are both irregular points of the space. As a matter of fact, a and b are both semiregular points of the space. Incidentally we have here a simple example of a semiregular space which is not regular. (Compare in this connection Example 3 above, and M. H. Stone, "Application of the theory of Boolean rings to General Topology," *Trans. Amer. Math. Society*, 1937, **41**, p. 452, where, the author who was the first to recognise the importance of semiregular spaces, has constructed a rather complicated example of a semiregular space which is not regular.)

In the space constructed above, a and b are U-inseparable and the other points are all regular. The space is H-closed. To prove this let us take an arbitrary open covering $\{G\}$ of R. Let us denote by $G(a)$, $G(b)$ a pair

of elements of $\{G\}$, which contain a and b respectively. $\overline{G(a)}$ and $\overline{G(b)}$ will each contain all but a finite number, say n and m respectively, of the c_i's. Suppose $n > m$. Then the c_i's which are not covered simultaneously by $\overline{G(a)}$ and $\overline{G(b)}$ will be n in number. These c_i's will be covered by the closures of a finite number of the G's, *say* $\overline{G}_1, \overline{G}_2, \ldots . \overline{G}_k$. It is easy to see that $R - [\overline{G(a)} + \overline{G(b)} + \overline{G}_1 + \overline{G}_2 + \ldots . + \overline{G}_k)]$ is a finite set of a_{ij}'s and b_{ij}'s. Hence, etc.

By a similar reasoning, we can show that the complement of every neighbourhood of a and b are H-closed. The complement of every neighbourhood of every a_{ij}, b_{ij}, c_i which are all regular points are also H-closed. Hence the condition of the theorem is satisfied in the space R and R is therefore maximal-Hausdorff. Being a Hausdorff irregular space, R cannot evidently be bicompact.

We have thus proved that a maximal-Hausdorff space need not necessarily be bicompact.

CHEMICAL EXAMINATION OF PLANT INSECTICIDES

Part IV. *Derris cuneifolia*

By N. V. Subba Rao and V. Subba Rao

(From the Departments of Chemistry and Chemical Technology, Andhra University, Waltair)

Received April 22, 1947

(Communicated by Prof. T. R. Seshadri, F.A.SC.)

Derris cuneifolia belongs to the section 'Euderris' to which *D. elliptica* and *D. ferruginea* belong. It is a robust climber with showy flowers and occurs in the eastern Himalayas, Nepal, Sikkim and Sylhet. The only earlier report on this species was from the Forest Research Institute, Dehra Dun, wherein it was stated that the roots contained less than 0·1% of rotenone.[1]

When the roots were tested directly by the Durham test, they did not give any indication for the presence of rotenoids. Detailed chemical examination was carried out on lines similar to those adopted for the other species of Derris.[2] From the various fractions, only one substance, now named 'cuneifolin', could be isolated. Rotenone was not obtained at any stage.

Cuneifolin is a pale yellow, crystalline substance melting at 180–81° and is only feebly toxic to fish.[3] It did not give the rotenoid colour reaction, nor did it give any test for flavones. From a consideration of analytical data and molecular weight, the molecular formula $C_{24}H_{24}O_5$ could be assigned to it. It was exceptional even amongst non-rotenoids isolated from leguminous plants in that it contained no methoxyl groups in spite of the high percentage of oxygen. Regarding the presence of hydroxyl groups it was neither soluble in alkali, nor did it give any ferric chloride colour indicating the absence of phenolic hydroxyl groups. This was supported by the fact that it did not give any methyl ether. However an acetate melting at 83–85° could be obtained, thereby indicating the presence of alcoholic groups. The analytical results agree with the mono-acetate. The substance however gave definite tests for a carbonyl group and yielded a dinitrophenyl-hydrazone. By hydrolysis with zinc and alkali, it formed a degradation product melting at 284° (charring) and exhibiting phenolic properties. Detailed study of this could not be done for lack of material.

Experimental

The roots of *D. cuneifolia* (450 g.) were powdered and extracted twice with ether in the cold. The solvent was completely removed and the residue (7·2 g.) repeatedly treated with petroleum-ether. The object of this treatment was to remove any fatty material present, but on concentrating the petroleum-ether washings, a crystalline solid (A) melting at 175–78° was deposited from it.

The resin left after washing with petroleum-ether was taken in a small amount of ether and set aside. From this a crystalline solid resembling (A) in melting point and other reactions separated and was filtered.

The filtrate was then extracted with 5% aqueous potassium hydroxide and the alkali-solubles were precipitated, taken in methyl alcohol and kept in an ice-chest. But no crystalline component separated from this. The alkali-insoluble ether solution after concentration deposited some more of the solid (A). The remaining portion of the neutral resin was taken in carbon tetrachloride and kept in the ice chest with a view to see whether any crystalline substance would separate. But none separated. Treatment with methyl alcoholic alkali also did not give any fruitful results.

The dried marc left behind after ether extraction was extracted with chloroform. The extract was small in amount. On treatment with ether, it yielded a crystalline component identical with the above (A). The total yield of the substance (A) was 1·0 gram.

Properties of the substance (A) (Cuneifolin)

After repeated crystallisations from acetone, it melted at 180–81°. It was pale yellow in colour and appeared under the microscope as hexagonal plates. The crystals were homogeneous and appeared to belong to one substance. Toxicity experiments were carried out with the substance using fish as test animals. In a concentration of 60 mg. per litre it produced definite toxic symptoms in fish (turning upside down) in 30 mins. In the Durham test it gave an orange colour with nitric acid but no blue or green colour with ammonia. It was soluble neither in alkali, nor in acid and it did not give any colour with ferric chloride. The substance was heated with gallic acid and sulphuric acid but no blue colour was obtained, thereby indicating the absence of a methylenedioxy group. By reduction with magnesium and hydrochloric acid no pink colour was formed. [Found: C, 73·5; H, 6·1; OCH_3, nil; molecular weight (Rast): 400; $C_{24}H_{24}O_5$ requires C, 73·5; H, 6·1%; molecular weight 392.]

Acetate.—Cuneifolin (0·1 g.) was boiled with acetic anhydride and a drop of pyridine for one hour. The acetate separated out on pouring the mixture into water; it was recrystallised from ethyl acetate and ethyl acetate-petroleum ether mixture. It was obtained as a colourless crystalline powder melting at 85–86°. [Found: C, 72·0; H, 5·8; $C_{24}H_{23}O_4$ (O.CO.CH_3) requires C, 71.9; H, 6.0%.)

The 2: 4 *di-nitro-phenyl-hydrazone* was obtained as a deep orange-red solid. It crystallised from methyl alcohol in the form of rhombohedral plates melting at 226–27°. [Found: C, 62·1; H, 5·0; $C_{24}H_{24}O_4$ [:N.NH.C_6H_3 $(NO_2)_2$] requires C, 62·9; H, 4·9%.]

The authors' thanks are due to Prof. T. R. Seshadri for his interest in their work and help and to Dr. S. Krishna of the Forest Research Institute, Dehra Dun, for the sample of *D. cuneifolia.*

Summary

Detailed chemical examination of the roots of *Derris cuneifolia* has been carried out. No rotenone could be obtained but a new crystalline compound could be isolated and is named ' Cuneifolin '. It has the molecular formula $C_{24}H_{24}O_5$ and contains an alcoholic hydroxyl group and a ketonic group.

References

1. Krishna and Ghose .. *Indian Forest Leaflet*, No. 2, 1942.
Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, (A), 1946, **24**, 344.
Murti, Rao and Seshadri .. *Ibid.*, (A), 1947, **25**, 22.

CHEMICAL EXAMINATION OF JACK TREE LATEX AND JACK FRUIT GUM

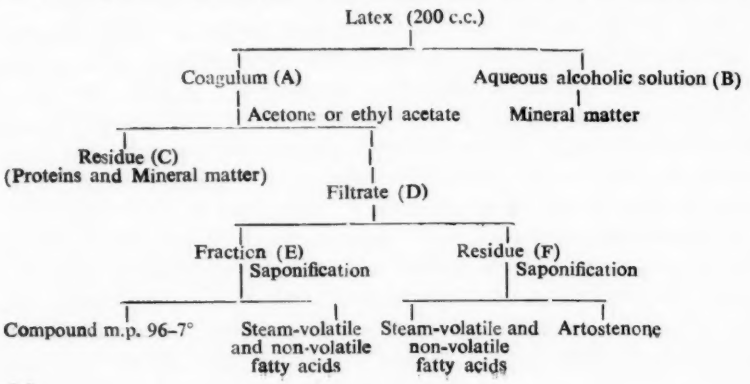
Part I. The Origin of Artostenone

By K. J. Balakrishna and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University, Waltair)

Received May 12, 1947

Jack tree (*Artocarpus integrifolia*) readily yields a milky latex when the green stem is cut or when a twig or leaf is broken off. During the war there was great interest in the study of plant latices and we had occasion to examine a small quantity of the Jack tree latex. It was coagulated by adding just enough of alcohol (equal volume) and the resulting coagulum (A) and aqueous alcoholic mother liquor (B) examined (see latex of *Calotropis gigantea*[1]). The latter (B) contained no special components. From the former (A) by treatment with acetone or ethyl acetate an insoluble portion (C) was separated and found to contain mineral salts and proteins. The acetone or ethyl acetate soluble portion (D) consisted mainly, of waxy matter. A sparingly soluble fraction (E) of this melted at 84°, gave no tests for sterols or resinols and on saponification yielded higher fatty acids and a substance melting at 96–7° and having the composition $C_{30}H_{58}O_2$. But the remaining fraction (F) gave strong reaction for sterols and on saponification yielded fatty acids, volatile as well as non-volatile. The unsaponifiable portion on repeated crystallisation provided a crystalline, sharp melting compound which was identified as artostenone[2] from a



detailed study of its properties and reactions. In the course of the preparation of an authentic sample of artostenone for purposes of comparison we also examined the gum obtained from the fruit and found that it closely resembled the tree latex in composition.

Thus artostenone is the main isolable crystalline component of the latex and fruit gum. Since it has been established to be a ketone with no hydroxyl group it should be occurring free and preliminary saponification of the waxy matter should not be absolutely necessary. But all attempts to isolate it from the waxy matter by simple crystallisation from various solvents were unsuccessful. Chromatography was next employed. Though free artostenone gets readily adsorbed on alumina, the waxy matter of the latex and gum was only very weakly adsorbed and no separation of artostenone could be effected. It therefore appeared that this ketone is not occurring free as such, but is present in a modified form capable of forming a wax ester.

In recent years enol esters of steroid ketones have been prepared by a number of workers[3] and it appeared to be possible that an enolic isomer of artostenone may be present in the waxy matter as an ester. The methods adopted by previous workers for preparing enol benzoates were examined but were found to produce no change in artostenone. But α-artostenone[2] which is obtained by the action of alcoholic sulphuric acid on artostenone readily forms an enol-benzoate. This enol-ester as well as α-artostenone undergo conversion into artostenone under the alkaline conditions prevalent during saponification. It therefore seems to be clear that artostenone does not occur in the plant, but α-artostenone in the form of wax esters is present and hence the need for the preliminary saponification during which the transformation into artostenone takes place.

In the course of this work we could isolate by repeated crystallisation a fairly sharp melting wax fraction which on saponification yields artostenone. But as in the case of other waxes this may be only a mixture of esters and not a simple substance. Among the acids volatile and non-volatile components have been found. The former are markedly offensive smelling indicating the existence of isovaleric acid. Definite tests for the presence of acetic acid are also given by this portion.

Experimental

Tree latex

The latex coming out of incisions on the trunk and branches of the tree was collected in bottles containing chloroform to prevent any possible decomposition. 200 c.c. of it was treated with an equal volume of alcohol

and the mixture stirred well and allowed to stand when a sticky solid settled down. The coagulum (A) was separated from the aqueous alcoholic solution (B) by filtration.

The coagulum (A) was dried in the sun (50 g.) and digested repeatedly with boiling ethyl acetate or acetone. As part of it was insoluble, the hot solution was filtered and the residue (C) on the filter was examined separately. The filtrate (D) was allowed to cool slowly when a colourless solid (E) separated out. It was filtered off and the filtrate was concentrated by removing the solvent under reduced pressure. The residue (F) was obtained as a sticky, brown semi-solid.

Fraction F

Attempts to crystallise this fraction from benzene-alcohol or acetone-alcohol mixture did not yield a crystalline product. It (25 g.) was therefore dissolved in benzene (150 c.c.), an equal volume of 8% alcoholic potash added and the mixture boiled under reflux for 20 hours. The solvents were distilled off on a water-bath and the concentrate was treated with water when a brown semi-solid separated out slowly. This unsaponifiable matter (10·0 g.) was extracted with ether and the ether solution was dried over anhydrous sodium sulphate. When the solvent was removed by distillation a reddish-brown semi-solid was left behind. It was dried in a vacuum desiccator over concentrated sulphuric acid and purified by repeated crystallisation from alcohol-acetone mixture, benzene-alcohol mixture and alcohol. It was thus obtained in the form of colourless large rectangular plates melting at 109°–110°; yield 1.5 g. (Found C, 85.0; H, 11.8; $C_{30}H_{50}O$ requires C, 84.5; H, 11.7%.)

The substance had all the properties and gave the colour reactions of artostenone (Nath[2]) and also formed an oxime melting at 175°. The mixed melting points of the ketone and of its oxime with authentic samples obtained from the fruit gum were not depressed.

The soap from the above saponification was decomposed with sulphuric acid. The fatty acids that were liberated were resolved into the steam-volatile and non-volatile fractions. The former had a markedly unpleasant odour resembling that of isovaleric acid and it also gave the lanthanum nitrate test for acetic acid. The non-volatile acids melted at about 65°.

Fraction E

On recrystallisation from ethyl acetate this was obtained as a hard nodular solid melting at 84°. It did not respond to the usual sterol or triterpene Colour reactions. Further purification through crystallistation did not bring

about any change either in its appearance or in its melting point. Hence it was saponified in benzene solution with alcoholic potash. The unsaponifiable matter, on repeated crystallisation from acetone and alcohol, was obtained as a well-defined crystalline (colourless tiny plates) compound melting at 96–7°. Further purification through crystallisation did not change either the melting point or the crystal structure. It did not respond to the characteristic colour reactions of sterols or resinols. However, it dissolved in concentrated sulphuric acid to produce a yellow solution exhibiting green fluorescence. The yield of the compound was small (0·2 g.) when compared with that of artostenone. (Found: C, 80.5; H, 13.4; $C_{30}H_{58}O_2$ requires C, 80.0; H, 13.0%.)

The soap from the above saponification was decomposed with sulphuric acid and the fatty acids were divided into steam-volatile and non-volatile fractions. The former closely resembled the fraction obtained from (F). The non-volatile acid mixture melted round about 80°.

Fraction C

The acetone or ethyl acetate insoluble portion was obtained in the form of a fine powder after drying for 2 or 3 days at room temperature. It was completely soluble in water and yielded about 8% of ash which contained phosphates and sulphates as acid radicals and calcium and iron as metallic radicals.

The organic part which was also soluble in water gave tests for proteins and the reactions showed that they belonged to the class of albumins and globulins.

Aqueous alcoholic solution (B)

When it was diluted with water no solid separated out. Further extraction with chloroform and ether did not yield any material. On acidifying it with hydrochloric acid there was no precipitate. The solution was found to contain mainly phosphates and sulphates as acid radicals and calcium and iron as metallic radicals.

Fruit gum

The gum was obtained from Malabar and was collected from the ripe fruit. It was dried first in the sun and then at 100° before use. It (250 g.) was fractionated and examined in detail exactly in the same manner as in the case of the coagulum (A) from the tree latex.

Extraction with ethyl acetate or acetone left behind fraction (C) consisting of mineral matter and proteins. These were similar to those obtained

in the corresponding fraction of the tree latex. The solution (D) on moderate concentration yielded fraction (E). This fraction, on saponification, yielded the compound melting at 96–7° and having the formula $C_{30}H_{58}O_2$. The yield of the compound in this case also was poor (0·5 g.). On removing the solvent completely under reduced pressure from the solution (D), fraction (F) (100 g.) was obtained. This was saponified. From the unsaponifiable matter (50 g.), 5 g. of pure artostenone could be obtained by repeated crystallisation. The steam-volatile and non-volatile acids from the soap solution were similar to those obtained from the corresponding fraction in the case of the tree latex.

Chromatography experiments

Artostenone (0.5 g.) was dissolved in benzene (50 c.c.) and was passed down a column (10 cm. by 1 cm.) of alumina under gentle suction. All the substance was adsorbed. Repeated elution with the same solvent brought out all the compound. It melted at 109–110° and no difference was found between different fractions.

The waxy solid fraction (F) (2 g.) was dissolved in benzene (100 c.c.) and subjected to chromatography as before. There was very poor adsorption and the portion adsorbed was also waxy like the unadsorbed matter though less pure. When the major unadsorbed portion was crystallised from a mixture of acetone and alcohol it was obtained as a colourless solid melting at 80–82°. This substance on saponification with alcoholic potash gave artostenone melting at 109–110°.

α-Artostenone

This was prepared according to the procedure of Nath[2], by heating artostenone with alcohol and sulphuric acid for 4 hours. When crystallised twice from alcohol it was obtained in the form of colourless glistening plates melting at 99–100°. The mixed melting point with artostenone was depressed (85–90°).

Reconversion of α-artostenone to artostenone

α-Artostenone (0.1 g.) was dissolved in 4% absolute alcoholic potash and the solution refluxed for four hours. The alcohol was removed by distillation and the residue treated with water. A colourless product separated out and it was filtered off. When crystallised twice from alcohol, it was obtained as shining rectangular plates melting at 109–110°; the mixed melting point with artostenone was undepressed.

α-Artostenone-benzoate

α-Artostenone (1.0 g.) was dissolved in pyridine (10 c.c.) and benzoyl chloride (10 c.c.) added. The mixture was refluxed for 20 minutes, cooled and treated with water. It was set aside until there was no smell of benzoyl chloride. The aqueous solution was then decanted off and the brown sticky solid left behind was stirred up with a little methyl alcohol. It was filtered and crystallised from a mixture of benzene and alcohol (1 : 3). The benzoate was obtained as clusters of fine colourless needles melting at 157–59° (Found: C, 83.5; H, 10.0; $C_{37}H_{54}O_2$ requires C, 83.8; H, 10.2%).

Hydrolysis of α-Artostenone-benzoate

α-Artostenone benzoate (0.5 g.) was dissolved in 5% alcoholic potash (10 c.c.) and the mixture was refluxed for 3 hours. The alcohol was removed by distillation and the residue taken up in water. The solid that separated out was filtered and washed free from alkali. On crystallisation from alcohol it melted at 109–110° and the mixed melting point with artostenone was undepressed.

Summary

Jack tree latex has the same composition as the fruit gum. Besides proteins and mineral substances, the two contain a high percentage of waxy matter. The less soluble portion (small amount) of the wax yields on saponification a non-steroid substance melting at 96–7° and having the probable composition of $C_{30}H_{58}O_2$. The more soluble major fraction yields artostenone on saponification. Experiments indicate definitely that this ketone is not occurring free and that it is formed as a result of the saponification. Though artostenone does not have the capacity of forming enol-esters, α-artostenone yields an enol-benzoate readily. Further α-artostenone and its enol-ester undergo conversion into artostenone under the conditions of saponification. Hence the conclusion is drawn that in the plant it is α-artostenone that occurs in the form of enol-wax-esters.

References

1. Murti and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1943, **18**, 145.
   Balakrishna, Rajagopalan and Seshadri .. *Ibid.*, 1945, **22**, 143.
2. Nath .. *Zeit. Physiol. Chem.*, 1937, B, **247**, 9–22.
3. Heilbron, *et al.* .. *J.C.S.*, 1938, 869.
   Ruzicka and Fischer .. *Helv. Chim. Acta.*, 1936, **19**, 806.
   Inhoffen .. *Ber.*, 1936, **69**, 2141.
   Westphal .. *Ibid.*, 1937, **70**, 2128.
   Ross .. *J.C.S.*, 1946, 737.

A NEW THEOREM ON THE TRANSFORMABILITY OF A LINE-ELEMENT INTO THE SPHERICALLY SYMMETRIC FORM

By K. R. Karmarkar

(J. K. Fellow, Benares Hindu University)

Received January 29, 1947

(Communicated by Professor V. V. Narlikar, F.A.SC.)

A spherically symmetrical line-element in its most general form may be expressed as follows:—

$$ds^2 = -A\,dr^2 - B\,(d\theta^2 + \sin^2\theta\,d\phi^2) + 2C\,dr dt + D\,dt^2, \tag{1}$$

where A, B, C, D are functions of r and t. Two of the equations of geodesics, when t is taken as the independent variable, are readily found to be

$$\frac{d^2\theta}{dt^2} + \frac{2}{r}\frac{dr}{dt}\cdot\frac{d\theta}{dt} - \sin\theta\cos\theta\left(\frac{d\phi}{dt}\right)^2 - P\frac{d\theta}{dt} = 0, \tag{2}$$

$$\frac{d^2\phi}{dt^2} + \frac{2}{r}\frac{dr}{dt}\frac{d\phi}{dt} + 2\cot\theta\,\frac{d\phi}{dt}\cdot\frac{d\theta}{dt} - P\frac{d\phi}{dt} = 0, \tag{3}$$

where

$$P = \tfrac{1}{2}(AD + C^2,^{-1})\left[(A\dot{A} + 2AC' - CA')\left(\frac{dr}{dt}\right)^2 + 2(AD' - CA)\frac{dr}{dt}\right.$$
$$\left. + (A\dot{B} + CB')\left\{\left(\frac{d\theta}{dt}\right)^2 + \sin^2\theta\left(\frac{d\phi}{dt}\right)^2\right\} + (A\dot{D} + 2C\dot{C} - CD')\right]$$
$$+ \left(\frac{2}{r}\frac{dr}{dt} - \frac{B'}{B}\frac{dr}{dt} - \frac{\dot{B}}{B}\right); \tag{4}$$

here dashes and dots indicate partial differentiation with respect to r and t respectively. From (2) and (3) we get

$$\frac{d^2\theta}{dt^2}\cdot\frac{d\phi}{dt} - \frac{d^2\phi}{dt^2}\cdot\frac{d\theta}{dt} - \sin\theta\cos\theta\left(\frac{d\phi}{dt}\right)^3 - 2\cot\theta\,\frac{d\phi}{dt}\left(\frac{d\theta}{dt}\right)^2 = 0. \tag{5}$$

It can be verified that this differential equation arises from the primitive

$$a\sin\theta\cos\phi + b\sin\theta\sin\phi + c\cos\theta = 0, \tag{6}$$

where a, b, c are arbitrary constants.

For an orthogonal line-element in pseudo-cartesian co-ordinates such as

$$ds^2 = -A\,(dx^1)^2 - B\,(dx^2)^2 - C\,(dx^3)^2 + D\,dt^2, \tag{7}$$

where A, B, C, D are functions of x^1, x^2, x^3, t, the condition (6) is equivalent to

$$ax^1+ bx^2+ cx^3= 0. \tag{8}$$

On eliminating a, b, c from (8) and the equations obtained by differentiating (8) twice with respect to t we have

$$\begin{vmatrix} x^1 & x^2 & x^3 \\ \frac{dx^1}{dt} & \frac{dx^2}{dt} & \frac{dx^3}{dt} \\ \frac{d^2x^1}{dt^2} & \frac{d^2x^2}{dt^2} & \frac{d^2x^3}{dt^2} \end{vmatrix} = 0. \tag{9}$$

The geodesics satisfy the equation

$$\frac{d^2x^\mu}{dt^2}+ \Gamma^\mu_{\alpha\beta}\frac{dx^\alpha}{dt}\cdot\frac{dx\beta}{dt}-\Gamma^4_{\alpha\beta}\cdot\frac{dx^\alpha}{dt}\cdot\frac{dx^\beta}{dt}\cdot\frac{dx^\mu}{dt}= 0\ (\mu= 1, 2, 3) \tag{10}$$

where x^4 means t. Substituting for the second derivatives in (9) from (10) we get

$$\begin{vmatrix} x^1 & x^2 & x^3 \\ \frac{dx^1}{dt} & \frac{dx^2}{dt} & \frac{dx^3}{dt} \\ \left[\Gamma^1_{\alpha\beta}- \Gamma^4_{\alpha\beta}\frac{dx^1}{dt}\right]\frac{dx^\alpha}{dt}\cdot\frac{dx\beta}{dt}- & \left[\Gamma^2_{\alpha\beta}- \Gamma^4_{\alpha\beta}\frac{dx^2}{dt}\right]\frac{dx^\alpha}{dt}\cdot\frac{dx\beta}{dt}- & \left[\Gamma^3_{\alpha\beta}- \Gamma^4_{\alpha\beta}\frac{dx^3}{dt}\right]\frac{dx^\alpha}{dt}\cdot\frac{dx^\beta}{dt} \end{vmatrix} = 0. \tag{11}$$

(11) must be true for all values of $\frac{dx^1}{dt}, \frac{dx^2}{dt}, \frac{dx^3}{dt}$.

This condition leads to the following equations:

(i) $\Gamma^2_{11}x^3 - \Gamma^3_{11}x^2= 0$, (ii) $\Gamma^3_{22}x^1-\Gamma^1_{22}x^3= 0$, (iii) $\Gamma^2_{33}x^1- \Gamma^1_{33}x^2= 0$; (12)

(i) $2\Gamma^3_{12}x^3- \Gamma^3_{11}x^1+ \Gamma^1_{11}x^3= 0$, (ii) $2\Gamma^3_{13}x^2+ \Gamma^2_{11}x^1- \Gamma^1_{11}x^2= 0$; (13)

(i) $2\Gamma^1_{12}x^3+ \Gamma^3_{22}x^2- \Gamma^2_{22}x^3= 0$, (ii) $-\Gamma^3_{23}x^1- \Gamma^1_{22}x^2+ \Gamma^2_{22}x^1= 0$; (14)

(i) $-2\Gamma^2_{32}x^1+ \Gamma^1_{33}x^3- \Gamma^3_{33}x^1= 0$, (ii) $-2\Gamma^1_{13}x^2- \Gamma^2_{33}x^3+ \Gamma^3_{33}x^2= 0$; (15)

$$2\Gamma^3_{23}x^2- 2\Gamma^2_{23}x^3- 2\Gamma^3_{13}x^1+ 2\Gamma^1_{14}x^3+ 2\Gamma^2_{14}x^1- 2\Gamma^1_{12}x^2= 0; \tag{16}$$

$$\Gamma^1_{14}= \Gamma^2_{24}= \Gamma^3_{34}; \tag{17}$$

$$\frac{\Gamma^1_{44}}{x^1}= \frac{\Gamma^2_{44}}{x^2}= \frac{\Gamma^3_{44}}{x^3}. \tag{18}$$

Combining (12 i) and (13) we get

$$\Gamma^2_{12}= \Gamma^3_{13}. \tag{19}$$

Similarly from (14), (15), (12 i) and (12 ii) we get

$$\Gamma^1_{12} = \Gamma^3_{32}; \quad \Gamma^1_{13} = \Gamma^2_{23}. \tag{20}$$

(19) and (20) make (16) an identity. (19) and (20) give on integration

$$\frac{B}{C} = \lambda\,(x^2, x^3, t); \quad \frac{C}{A} = \mu\,(x^1, x^3, t);$$

$$\frac{A}{B} = \nu\,(x^1, x^2, t),$$

where λ, μ, ν are arbitrary functions of the variables indicated. From these it may be safely concluded that

$$A = \alpha\,(x^1, t)\,P; \quad B = \beta\,(x^2, t)\,P; \quad C = \gamma\,(x^3, t)\,P, \tag{21}$$

where P is any function of x^1, x^2, x^3, t and α, β, γ are arbitrary functions). Substituting these in (12) we get

$$\frac{\partial P}{\partial x^1}(\alpha\, x^1)^{-1} = \frac{\partial P}{\partial x^2}(\beta\, x^2)^{-1} = \frac{\partial P}{\partial x^3}(\gamma\, x^3)^{-1}.$$

Using the last result in (13 i) we get $\frac{\partial \alpha}{\partial x^1} = 0$. Similarly from (14) and (15) we get $\frac{\partial \beta}{\partial x^2} = \frac{\partial \gamma}{\partial x^3} = 0$. Thus α, β, γ, are functions of t only. From (17) we get $\frac{\alpha}{\beta} = \frac{1}{l^2}$ and $\frac{\alpha}{\gamma} = \frac{1}{m^2}$, where l and m are arbitrary constants. Thus we get

$$B = l^2 A; \quad C = m^2 A. \tag{22}$$

Equations (12) now give

$$\frac{\frac{\partial A}{\partial x^1}}{A x^1} = \frac{\frac{\partial A}{\partial x^2}}{A x^2 l^2} = \frac{\frac{\partial A}{\partial x^3}}{A x^3 m^2}. \tag{23}$$

Integrating these we get

$$A = \phi\,[\{(x^1)^2 + l^2\,(x^2)^2 + m^2\,(x^3)^2\}, t]. \tag{24}$$

Equations (18) now give

$$\frac{\frac{\partial D}{\partial x^1}}{x^1} = \frac{\frac{\partial D}{\partial x^2}}{x^2 \cdot l^2} = \frac{\frac{\partial D}{\partial x^3}}{x^3 m^2}.$$

Integrating these we get

$$D = \psi\,[\{(x^1)^2 + l^2\,(x^2)^2 + m^2\,(x^3)^2\}, t]. \tag{25}$$

A simple transformation

$$x^1 = x^1; \quad l x^2 = x^2; \quad m x^3 = \bar{x}^3; \quad t = t,$$

gives us the result

$$A = B = C = \phi\ [\{(x^1)^2 + (x^2)^2 + (x^3)^2\},\ t],$$

$$D = \psi\ [\{x^1)^2 + (x^2)^2 + (x^3)^2\},\ t].$$

This proves that the line-element is a simple transform of a spherically symmetrical line-element.

The above investigation is a logical sequel to the work recently reported in these *Proceedings* by Prof. V. V. Narlikar[1] and the author. It provides a necessary and sufficient condition relating to the geodesics that an orthogonal line-element in pseudo-cartesian co-ordinates x^1, x^2, x^3 and time t may be transformable into a spherically symmetrical form.

The author should like to acknowledge his indebtedness to Professor V. V. Narlikar for the guidance that he has received in the preparation of this note.

Summary

The differential equations for the geodesics of a general spherically symmetrical line-element of the form, $ds^2 = -A\,dr^2 - B\,(d\theta^2 + \sin^2\theta d\phi^2) + 2C\,dr\,dt + D\,dt^2$, are shown invariably to admit an integral of the form, $a \sin\theta \cos\phi + b \sin\theta \sin\phi + c \cos\theta = 0$, where a, b, c are arbitrary constants. It is further shown that if the corresponding equations for a general line-element of the form, $ds^2 = -A\,(dx^1)^2 - B\,(dx^2)^2 - C\,(dx^3)^2 + D\,dt^2$, admit an integral of the type $ax^1 + bx^2 + cx^3 = 0$, the line-element is a transform of a spherically symmetrical line-element. Thus a necessary and sufficient condition for an orthogonal line-element in pseudo-cartesian co-ordinates x^1, x^2, x^3, and t to be a transform of a spherically symmetrical line-element is that the geodesics satisfy the equation $ax^1 + bx^2 + cx^3 = 0$.

References

[1] Narlikar, V. V., and K. R. Karmarkar .. *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 451–55.

CHEMICAL EXAMINATION OF THE SEEDS OF *DODONAEA VISCOSA*

Isolation of Dodonin, Dodogenin and a Fixed Oil

By Dharam Bal Parihar and Sikhibhushan Dutt, F.A.Sc.

(*Department of Chemistry, Delhi University*)

Received March 5, 1947

Dodonea viscosa or Benmendu as it is known in Punjabi and Aliar in Hindi is an ever-green shrub belonging to the natural order of Sapindaceæ. It is met with throughout India, often growing wild, but generally cultivated in the form of a hedge for ornamenting gardens, roads, etc., and is also clipped into various artistic designs for this purpose. It is particularly abundant in the Punjab, United Provinces, Central Provinces, Bengal, Andhra Districts and Ceylon. In sheltered and moist places the plant is often found as a small tree with erect twiggy branches, but commonly it is a shrub from nine to twelve feet high.

The plant possesses a great repute in medicine. According to Kirtikar and Basu,[1] the leaves of the plant are used in baths and fomentations, and their powder is applied over wounds, burns and scalds. They are also considered to be very efficacious in rheumatism and possess great febrifugal properties. In the Punjab, the leaves made into a paste are applied in snake-bite. In South Africa the infusion of the green plant is often given in stomach disorders. In Peru the leaves are chewed like Coca leaves as a stimulant. The seeds of the plant also are reputed to have similar properties, as the leaves.

Since no work has been done on this plant and also in view of its medicinal importance, the present work was undertaken to find out the active principles present in the seeds, by systematic chemical examination.

The present authors working on the seeds of the plant have been able to isolate two compounds, one a glucoside melting at 182–86° C., and the other a deep yellow fixed oil in yields of 3·42 and 20·27% respectively. The systematic chemical examination of the fixed oil will be the subject of a separate communication, while in the present one the glucoside and particularly the product of its hydrolysis have been studied in detail.

The glucoside and the product of its hydrolysis have been named "Dodonin" and "Dodogenin" respectively. As Dodonin could not be

purified further, Dodogenin was made the subject of detailed study. It crystallises in fine small needles melting at 249° C., and has a molecular formula $C_{23}H_{36}O_5$. Dodogenin definitely contains a cyclopentenophenanthrene nucleus in the molecule as was found by Selenium dehydrogenation of the compound, when it gave the Diel's Hydrocarbon ($C_{18}H_{16}$). It does not contain any phenolic hydroxy group, but the presence of five alcoholic hydroxyls has been confirmed owing to the formation of penta-acetyl, penta-benzoyl and penta-*p*-nitrobenzyl derivatives.

Experimental

9·96 Kilos of the powdered seeds of the plant were extracted with petroleum ether (B.P. 40°–60° C.) in the cold in order to get rid of the fatty matter from the seeds. On distilling off the solvent a deep yellow fixed oil in an yield of 20·27% was obtained. The seeds after extraction with cold petroleum ether were next extracted with hot ethyl alcohol under reflux in lots of 1 Kilo at a time. The extracts were filtered hot and the solvent distilled off on a water-bath. The syrupy mass was allowed to stand overnight when some solid product settled down. This was filtered off and washed with ether. The mass was repeatedly dissolved in alcohol and precipitated with ether in order to free it from sugars. Thus 341 gm. of the material was obtained in white microneedles melting at 182–86° C., in an yield of 3·42%. The substance has been named " Dodonin ".

Dodonin is very bitter in taste. It dissolves easily in water producing lathers. It is soluble in methyl and ethyl alcohols, acetic acid and phenol, while insoluble in benzene, ether and petroleum ether. It reduces Fehling's Solution readily.

As dodonin could not be obtained in quite pure form, it was hydrolysed by boiling with 5% HCl and the mass was allowed to cool when a crystalline precipitate settled down. It was filtered and repeatedly washed with water. It was then purified by treatment with animal charcoal in alcohol. Dodogenin was finally crystallised from alcohol-benzene mixture (1 : 4) in fine white needles melting sharp at 249° C.

Both Dodonin and Dodogenin are saturated compounds and thus do not add bromine. They neither reduce ammonical silver-nitrate, nor give Legal's test. Both the compounds give Liebermann-Burchard's and Salkowski's reactions promptly, indicating the presence of sterol nucleii in the molecules. They are insoluble in alkalies and do not give any colour with them. None of them give any colour with ferric chloride.

Dodogenin is soluble in methyl and ethyl alcohols. It is insoluble in water, acetone, chloroform, benzene, ether and petroleum ether. It also dissolves in acetic acid and pyridine easily. Dodogenin is insoluble in hot or cold HCl, and does not contain nitrogen in the molecule. It gives deep red colour with conc. H_2SO_4. (Found: C= 62·73, 62·28, 62·79; H= 8·16, 8·06, 8·11 per cent.; M.W. Cryoscopic in phenol= 439·91, 440·82, 440·14; $C_{23}H_{36}O_8$ requires C= 62·72, H= 8·18 per cent.; M.W. 440.)

Acetylation of Dodogenin.—2 gm. of Dodogenin were dissolved in 5 c.c. of acetic anhydride, and to it 0·5 gm. of anhydrous sodium acetate were added. The mixture was refluxed in a boiling tube for about half an hour on the sand-bath. After this the hot mixture was poured into cold water. The compound which separated in fine crystalline form, was filtered and washed with water. It was recrystallised from alcohol-benzene mixture (1 : 2) in small needles melting at 190° C. It is soluble in ethyl and methyl alcohols, ethyl acetate and chloroform, while insoluble in water, benzene, ether and petroleum ether. (Found: C= 60·89, 60·90; H= 7·09, 7.06 per cent.; $COCH_3$ = 33.32%; $C_{23}H_{31}O_8$ $(COCH_3)_5$ requires C= 60·92; H= 7·07%, and $COCH_3$ calculated for five acetyl groups in the molecule = 33·07%.)

Benzoylation of Dodogenin.—To a solution of 1 gm. of Dodogenin in 10 c.c. of pyridine, 5 c.c. of benzoyl chloride were added. The mixture was allowed to reflux for about half an hour on the sand-bath. The contents, while hot, were poured into cold water and kept overnight when a crystalline mass settled down. It was treated with excess of sodium carbonate solution, filtered and thoroughly washed with water. After drying, the product was recrystallised from ethyl acetate in small cubes and plates melting at 135° C. The benzoyl compound is soluble in alcohols, chloroform, and hot ethyl acetate, while quite insoluble in water, benzene, ether and petrol-ether. (Found: C= 72·55, 72·49; H= 5·89, 5·84; $C_{23}H_{31}O_8$ $(COC_6H_5)_5$ requires C= 72·50, H= 5·83%.)

p-Nitrobenzyl derivative.—To 1 gm. of Dodogenin dissolved in 5 c.c. of pyridine were added 2 gm. of *p*-nitrobenzyl chloride, and the mixture was refluxed on the sand-bath for about half an hour. On cooling, the crystalline mass, which settled down, was filtered, rapidly washed with alcohol and dried. The compound was recrystallised from alcohol-ether mixture (5 : 1) in very small needles melting at 165° C. It is soluble in alcohol and ethyl acetate, while insoluble in water, benzene, chloroform, acetone, ether and petrol-ether. (Found: C= 62·39, 62·41; H= 5·46 5·550; $C_{58}H_{61}N_5O_{18}$ requires C= 62·42; H= 5·47%.)

Methylation of Dodogenin.—A suspension of 2 gm. of the substance in 200 c.c. of anhydrous acetone was treated with 8 c.c. of freshly distilled dimethyl sulphate and 20 gm. of anhydrous potassium carbonate. After refluxing for 30 hours on a water-bath the contents were cooled, filtered, and the residue washed with a little acetone. From the filtrate the solvent was distilled off and excess of water was added to the syrupy residue, when a crystalline mass settled down. It was filtered and washed with water. The compound was recrystallised from hot ethyl acetate in glistening rhombic needles melting at 132° C. The methylated derivative is soluble in acetone while Dodogenin is not. It is soluble in alcohol, chloroform and ethyl acetate, while insoluble in water, benzene, ether and petrol-ether. [Found: C= 65·90, 65·87; H= 9·11, 9·06; percentage of OCH_3= 30·41, 30·38 $C_{23}H_{31}O_3$ $(OCH_3)_5$ requires C= 65·88, H= 9·01; OCH_3 calculated for five methoxyl groups 30·39%.]

Selenium dehydrogenation of Dodogenin.—5 gm. of Dodogenin were intimately mixed with 25 gm. of Selenium metal powder and the mixture was taken in a combustion tube. The mixture was heated first at a lower temperature, while a slow current of dry hydrogen was passed through the tube. The temperature was gradually raised to 310° C., and the furnace was maintained at that temperature for about an hour. The compound, which sublimed in the receiver in orange-red plates was recrystallised from alcohol with the addition of a little ether in glistening orange-red plates melting at 122° C. It was found to be the Diel's Hydrocarbon ($C_{18}H_{16}$).

Fusion with NaOH.—2 gm. of the compound were gradually added to a molten mixture of 20 gm. of caustic soda and 1 c.c. of water in a nickel crucible maintained at 200° C. The reaction was vigorous and a lot of frothing took place during the reaction. The mass was finally heated at 00° C. for half an hour. The reaction was over when carbon dioxide was no longer evolved. The cold melt was dissolved in water and neutralised with dilute hydrochloric acid, when a white crystalline precipitate settled down, which was filtered, washed and dried. It was then crystallised from methyl alcohol in fine micro-needles melting at 224° C. It does not give any colour with ferric chloride. It is soluble in sodium hydroxide and carbonate solutions. It appears to be a carboxylic acid. It is also soluble in hot ethyl and methyl alcohols, and ethyl acetate, while insoluble in acetone, water and chloroform. (Found: C= 58·07, 58·11; H= 8·32, 8·30%; $C_{18}H_{34}O_8$ requires C= 58·7, H= 8·7%.)

Further work on the subject is in progress.

Summary and Conclusion

1. From the seeds of *Dodonæa viscosa* a glucoside (M.P. 182–86° C.) and a fixed oil have been obtained in yields of 3·42 and 20·27 per cent. respectively.

2. The glucoside and the product of its hydrolysis have been named " Dodonin " and " Dodogenin " respectively.

3. " Dodogenin " which has a molecular formula $C_{23}H_{36}O_8$ melts at 249° C. and contains a cyclo-penteno-phenanthrene nucleus in its molecule. In general properties it resembles the Sapogenins.

4. A number of derivatives of " Dodogenin " have been prepared and examined.

References

1. Kirtikar and Basu .. *Indian Medicinal Plants*, **1**, 641-43.

STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXVIII. The Camphor-β-sulphonates (*d*-, *l*- and *dl*-) of α-Amino-pyridine, α-Amino thiazole, *p*-Amino benzene sulphonyl amido-2-pyridine and 6-Methoxy-8-amino quinoline

By Bawa Kartar Singh, F.A.Sc., and Kanwar Maghar Singh Manhas

(Punjab University Institute of Chemistry, Lahore, and Department of Chemistry, University of Allahabad, Allahabad)

Received April 16, 1947

In Parts XXIII and XXV of this series of investigations,[1] the rotatory dispersions of salts of camphor-β-sulphonic acids (*d*-, *l*- and *dl*-) were described. We have included in the present investigation heterocyclic bases and a sulpha drug, namely, *p*-amino benzene sulphonyl amido-2-pyridine.

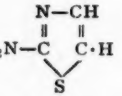
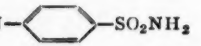
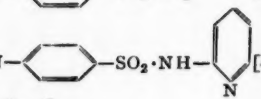
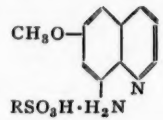
One of the objects in preparing these sulphonates was to obtain water-soluble sulphonamides. *p*-Amino benzene sulphonamide is very insoluble in water (1 in 200 at 25° C.) but its camphor-β-sulphonates are very soluble. One of the main difficulties in the parenteral administration of sulphonamides is their very sparing solubility in water. If they are administered orally the danger from the formation of uroliths in the kidney as well as the blocking of the urinary passage has to be guarded against. Smyth and Carpenter[2] in their study of the pharmacological action of *p*-amino benzene sulphonamide-*d*-camphor-β-sulphonates found that the salt was equally effective as the free sulphonamide, although it contained only 42·5% of the base.

It is well known that optically active and opposite isomers have very different action on living organism: *l*-Hyoscy amine was found by Cushney[3] to be twice as powerful in paralysing the vagus, as the racemic form Atropine, and twenty times as active as the dextro isomer. In Part XXV one of us has described the water-soluble camphor-β-sulphonates of *p*-amino benzene sulphonamide. The pharmacological action of this salt as well as of the salts described in this paper are under investigation and will form the subject of a further communication.

Nature of Rotatory Dispersion

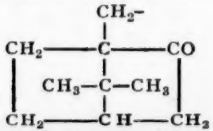
The compounds described in this paper exhibit simple rotatory dispersion as their rotatory power can be expressed by Drude's one term equation $[\alpha]=\frac{k_0}{\lambda^2-\lambda_0^2}$. The calculated values of rotatory power (c) for

TABLE I

No.	Structural formula		$[M]_D^{35°}$					
			Water (80)*	Methyl alcohol (31·2)	Pyridine (12·4)	Ethyl alcohol (25·8)	Acetone (21·5)	Chloroform (5·2)
†1	‡R·$SO_3H·H_2N$ —	[325][a]	66·64 (11·05)[b]	105·3 (20·43)	117·3 (24·60)	118·3 (22·74)	..	147·2 (30·15)
2	R. $SO_3H·H_2N$ —	[326]	60·32 (14·23)	94·54 (22·67)	107·6 (26·62)	109·1 (26·99)	..	130·4 (31·20)
3	R. $SO_3H·H_2N$ — 	[332]	63·08 (13·78)	101·3 (25·44)	108·8 (27·81)	119·5 (30·34)	..	146·1 (37·21)
4†	R. $SO_3H·H_2N$ — 	[404]	68·57 (11·28)	113·2 (18·47)	135·2 (22·68)	..	..	..
5	R. $SO_3H·H_2N$ — 	[481]	..	96·18 (23·78)	..	108·2 (24·16)	120·2 (27·00)	..
6		[406]	52·77 (13·37)	91·35 (21·42)	103·0 (24·0)	113·7 (24·89)	125·9 (24·84)	164·4 (33·64)

* Values of dielectric constants are given in brackets.

† The values of M × K/100 for (1) and (4) are calculated from data of Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, (A), 1945, **22**, 84.

‡ R = $C_{10}H_{15}O$ or 

[a] The values in brackets refer to molecular weights.

[b] The values in brackets refer to molecular rotation constant, M × K./100, in Drude's equation.

TABLE II

No.	Camphor-β-sulphonate of	Concentration in gm./100 c.c.	$[M]_{\lambda}^{35°}$ in aqueous solution											
			Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 5403	Hg 4358
1	α-Amino thiazole	1·0000	42·42	47·63	55·86	62·07	66·00	79·68	94·32	103·2	131·0	147·0	159·1	212·5
2	α-Amino pyridine	1·0000	41·63	46·49	53·86	59·57	63·02	74·91	87·26	94·61	116·5	128·6	137·4	173·7
3	6-Methoxy-8-amino quinoline	1·0000	37·91	..	48·72	53·63	56·52	66·79	77·18	..	..	..	..	..

different wave-lengths agree with the observed rotations (*o*). The differences between the observed and the calculated values of rotations were of the nature of casual experimental errors. The calculated values (*c*) and the differences ($o - c$) are omitted from the Tables (III to VI) for the sake of economy of space. In 355 observations out of 374, the rotations of the dextro and lævo forms differ from the calculated values within 0·02° of the observed angle of rotation, and in the remaining cases, the difference is about 0·03°.

These observations (Tables III to VI) further support Pasteur's principle of Molecular Dissymmetry as the values of rotatory powers of the *d*- and *l*- form are identical within the limits of experimental error.

THE EFFECT OF SOLVENT ON THE ROTATORY POWER

The molecular rotatory power, $[M]_D^{35°}$, of the compounds in different solvents is given in Table I. The sequence of decreasing rotatory power of the salts of the different bases is given below:

(*a*) 6-*Methoxy*-8-*amino quinoline.*

Chloroform > Acetone > Ethyl alcohol > Pyridine > Methyl alcohol > Water.

The sequence agrees with that of their dielectric constants in the reverse order except that for pyridine and acetone.

(*b*) α-*Amino thiazole.*

Chloroform > Ethyl alcohol > Pyridine > Methyl alcohol > Water.

The sequence is again in the reverse order of their dielectric constants except for pyridine.

(*c*) α-*Amino pyridine.*

Chloroform > Pyridine > Ethyl alcohol > Methyl alcohol > Water.

The above order of decreasing rotatory power is exactly in the reverse order of their dielectric constants.

CH_3——CH——CH_2

[a] The values in brackets refer to molecular weights.
[b] The values in brackets refer to molecular rotation constant, M × K./100, in Drude's equation.

TABLE III. *6-Methoxy-8-amino quinolino-camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Pyridine		Ethyl alcohol		Acetone		Chloroform	
Concentration in gm./100 c.c.	*d*- 1·0000		1·0000		1·0000		1·0000		0·5000		1·0000	
	l- 1·0000		1·0000		1·0000		1·0000		0·5000		1·0000	
Calculated $[\alpha]_{\lambda_0}$	$\pm \frac{3\cdot294}{\lambda^2 - \cdot098}$ 0·3130		$\pm \frac{5\cdot277}{\lambda^2 - \cdot1095}$ 0·3310		$\pm \frac{5\cdot911}{\lambda^2 - \cdot1159}$ 0·3404		$\pm \frac{6\cdot13}{\lambda^2 - \cdot1225}$ 0·3500		$\pm \frac{6\cdot365}{\lambda^2 - \cdot1469}$ 0·3833		$\pm \frac{8\cdot265}{\lambda^2 - 0\cdot1442}$ 0·3798	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Cd_{4678} ..	..	..	..	..	+57·50°	−57·50°	..	..	..	..	..	..
Cd_{4800} ..	..	..	..	..	51·50	51·00	..	..	..	..	..	..
Cd_{5086} ..	..	..	..	..	41·50	42·00	..	..	..	..	..	..
Ag_{5209} ..	+18·50°	−19·00°	..	..	38·00	38·00	..	..	..	..	..	..
Hg_{5461} ..	16·50	16·50	..	..	32·50	32·50	..	..	..	..	..	..
Hg_{5780} ..	14·50	14·50	+24·00°	−23·50°	27·00	27·00	+29·09°	−29·00°	+34·00°	−34·00°	+43·50°	−43·50°
Na_{5893} ..	13·00	13·50	22·50	22·00	25·50	25·00	28·00	28·00	31·00	32·00	40·50	41·00
Li_{6104} ..	12·50	12·00	20·00	19·50	22·50	23·00	24·50	24·00	28·00	28·00	36·00	36·50
Li_{6708} ..	9·50	9·00	15·50	15·50	17·00	17·50	19·00	18·50	22·00	21·00	27·00	27·00
	No mutarotation		No mutarotation		No mutarotation		Hg_{5780} line could not be read after 24 hours		No mutarotation		No mutarotation	

TABLE IV. *α-Amino thiazole camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Pyridine		Ethyl alcohol		Chloroform	
Concentration in gm./100 c.c.	*d-* 1·0000		1·0000		1·0000		1·0000		1·0000	
	l- 1·0000		1·0000		1·0000		1·0000		1·0000	
Calculated $[\alpha]_{\lambda_0}$	$\pm \frac{4\cdot155}{\lambda^2-0\cdot1251}$ 0·3537		$\pm \frac{7\cdot664}{\lambda^2-\cdot09649}$ 0·3106		$\pm \frac{8\cdot377}{\lambda^2-\cdot09145}$ 0·3024		$\pm \frac{9\cdot141}{\lambda^2-\cdot09539}$ 0·3088		$\pm \frac{11\cdot206}{\lambda^2-\cdot0926}$ 0·3043	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Hg_{4358} ..	+64·00°	−63·00°	+83·50°	−82·50°	+84·50°	−86·00°	+95·00°	−96·00°	+116·00°	−115·50°
Li_{4603} ..	47·50	48·00	67·00	66·50	70·00	69·50	79·50	78·50	93·50	94·00
Cd_{4678} ..	44·00	45·00	63·50	63·00	66·50	66·00	75·00	74·00	88·00	89·50
Cd_{4800} ..	40·00	40·00	57·00	57·00	60·00	60·50	67·00	67·50	82·50	81·00
Cd_{5086} ..	31·00	31·50	47·50	47·00	50·00	50·50	56·00	56·00	69·00	68·00
Ag_{5209} ..	28·50	28·50	44·00	43·50	47·00	46·50	51·00	52·00	63·00	62·00
Hg_{5461} ..	24·00	24·00	38·00	38·00	40·50	40·50	45·00	45·00	54·50	54·50
Hg_{5780} ..	20·00	20·00	32·00	32·50	34·50	34·50	38·00	38·50	46·50	46·50
Na_{5893} ..	19·00	18·50	30·50	30·50	33·00	33·00	36·00	36·50	44·00	44·00
Li_{6104} ..	17·00	16·50	27·50	27·00	30·00	29·00	33·00	33·00	40·00	40·00
Cd_{6438} ..	14·50	13·50	25·00	25·00	26·00	25·50	29·50	29·00	35·00	35·50
Li_{6708} ..	12·50	12·00	22·00	22·00	23·50	23·00	26·00	25·50	30·50	31·50
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE V. *α-Aminopyridino-camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine		Chloroform	
Concentration in gm./100 c.c. $\begin{cases} d- \\ l- \end{cases}$	1·0000 1·0000		1·0000 1·0000		1·0000 1·0000		1·0000 1·0000		1·0000 1·0000	
Calculated $\begin{cases} [\alpha] \\ \lambda_0 \end{cases}$	$\pm \frac{4\cdot367}{\lambda^2 - \cdot1082}$ 0·3289		$\pm \frac{6\cdot954}{\lambda^2 - 0\cdot1052}$ 0·3243		$\pm \frac{8\cdot165}{\lambda^2 - 0\cdot1013}$ 0·3183		$\pm \frac{8\cdot279}{\lambda^2 - \cdot1009}$ 0·3176		$\pm \frac{9\cdot57}{\lambda^2 - \cdot1068}$ 0·3268	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d-	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Hg_{4358} ..	+53·50°	−54·50°	+82·50°	−83·50°	+92·00	−94·00	+93·00°	−93·50	+115·00	−117·00
Li_{4603} ..	42·00	42·50	65·50	66·50	74·00	73·00	74·50	74·00	91·00	91·50
Cd_{4678} ..	39·00	39·50	61·00	62·00	70·00	71·00	70·00	70·50	85·00	85·00
Cd_{4800} ..	36·00	35·00	55·50	55·00	63·00	63·50	64·00	64·00	77·50	77·50
Cd_{5086} ..	29·00	29·00	45·00	45·00	52·00	52·00	52·50	52·50	63·00	62·50
Ag_{5209} ..	26·50	26·50	42·00	41·50	48·00	48·50	48·50	48·00	58·00	58·00
Hg_{5461} ..	23·00	23·00	36·00	36·00	41·50	41·50	42·00	42·00	50·00	50·00
Hg_{5780} ..	19·50	19·50	30·50	30·00	35·00	35·50	35·50	35·00	42·00	42·00
Na_{5893} ..	18·50	18·00	29·00	28·50	33·00	33·00	33·50	33·50	40·00	39·50
Li_{6104} ..	16·50	17·00	26·00	26·50	30·00	29·50	30·50	30·00	36·00	36·00
Cd_{6438} ..	15·00	14·00	22·00	21·00	27·50	26·00	27·00	26·00	30·00	32·00
Li_{6708} ..	13·00	12·50	20·00	19·50	24·00	23·00	23·50	23·00	28·00	27·50
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE VI

p-*Amino benzene sulphonyl amido-2-pyridino camphor-β-sulphonates*

Solvent		Methyl alcohol		Ethyl alcohol		Acetone	
Concentration in gm./100 c.c.	*d-*	1·0000		1·0000		0·5000	
	l-	1·0000		1·0000		0·5000	
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{4\cdot945}{\lambda^2 - \cdot1004}$ 0·3168		$\pm \frac{5\cdot024}{\lambda^2 - \cdot1188}$ 0·3447		$\pm \frac{5\cdot613}{\lambda^2 - \cdot1199}$ 0·3463	
Line		Obs. [α]		Obs. [α]		Obs. [α]	
		d-	*l-*	*d-*	*l-*	*d-*	*l-*
Hg_{4358}	..	+55·00°	−55·50°	+70·00°	−71·00°	+81·00	82·00°
Li_{4603}	..	44·00	44·00	54·00	54·00	61·00	62·00
Cd_{4678}	..	42·00	42·50	51·00	50·00	55·00	55·00
Cd_{4800}	..	37·50	37·50	44·00	43·50	49·00	50·00
Cd_{5086}	..	30·50	30·50	36·50	37·00	40·00	40·00
Ag_{5209}	..	29·00	28·50	33·50	33·00	36·00	36·00
Hg_{5461}	..	25·00	25·00	28·00	28·00	32·00	32·00
Hg_{5780}	..	22·00	22·00	24·00	24·00	27·00	28·00
Na_{5893}	..	20·00	20·50	22·50	22·50	25·00	25·00
Li_{6104}	..	18·00	18·50	19·50	19·00	23·00	21·00
Cd_{6438}	..	16·00	15·50	18·00	17·50	20·00	19·00
Li_{6708}	..	14·50	14·00	15·00	15·00	17·00	17·00
		No mutarotation		No mutarotation		No mutarotation	

(*d*) p-*Amino benzene sulphonyl amido-2-pyridine.*

Acetone> Ethyl alcohol> methyl alcohol.

The order of decreasing rotatory power in this case is exactly in the reverse sequence of their dielectric constants.

As already pointed out in our previous work[4] it will be more rational to compare the rotatory power of the solutions with their dielectric constants and not with the dielectric constants of the solvents.

THE MOLECULAR ROTATORY DISPERSION OF THE SALTS OF CAMPHOR-β-SULPHONIC ACIDS IN AQUEOUS SOLUTION AND THE VALUE OF MOLECULAR ROTATORY POWER OF CAMPHOR-β-SULPHONATE ION IN WATER

Table II gives values of $[M]_{\lambda}^{35°}$ for λ varying from 4358 Å.U. to 6708 Å.U. for the different camphor-β-sulphonates in aqueous solution. If the salts are completely ionised in dilute aqueous solution, their molecular rotations will be practically the same for a given wave-length, the rotation being independent of the inactive basic ion: in concentrated solution the

observed molecular rotation may be greater or less than the value in dilute solution, because it is due both to the active ion and to the non-ionised molecule. The results given in Table II show that 6-methoxy-8-amino quinoline salt has $[M]_D^{35°} = 53{\cdot}63°$ which is identical with the mean value of $[M]_D^{35°} = 53.6°$ for the acid ion.[5] The molecular rotatory power of salts of α-amino thiazole is 62·1° and of α-amino pyridine 59·6° for sodium D-line in 1% solution. It, therefore, follows that whereas the camphor-β-sulphonates of 6-methoxy-8-amino quinoline are completely electrolytically dissociated, the other two salts are not so. The molecular rotatory power of the camphor-β-sulphonic ion in water being 53°–54° at 35° C., the observed rotation of camphor-β-sulphonates of α-amino pyridine and α-amino thiazole indicate that the undissociated salts have higher rotatory power than the completely dissociated molecule.

The Relation between Chemical Constitution and Rotatory Power

In Table I the molecular rotatory powers $[M]_D^{35°}$ of different compounds in six solvents are given. It is seen that the aniline salt (1) has higher rotatory power than that of the salt of α-amino pyridine (2). The molecular weights of the two salts are practically the same. It is thus clear that the nitrogen in the pyridine ring has depressed the rotatory power. The molecular rotatory power of α-aminothiazole camphor-β-sulphonate (3) is higher than that of the salt of α-amino pyridine (2). This shows that the thiazole ring has a higher rotatory effect than the pyridyl nucleus. The rotatory power of the thiazole salt is practically the same as that of the aniline salt except in methyl alcohol and pyridine in which it is slightly lower. *p*-Aminobenzene sulphonamido camphor-β-sulphonate (4) has higher rotatory power in methyl alcohol than that of the camphor-β-sulphonate of *p*-aminobenzene sulphonylamido-2-pyridine (5). This further shows that the pyridyl radical has a depressing effect on rotatory power for the sodium D-line. The above mentioned sequence, however, does not hold good for other wave-lengths. It is, therefore, necessary for any strict comparison of rotatory powers of a series of compounds that the effects of dispersion should be eliminated. This elimination is not easy when the dispersion is complex but when a linear relationship is found to hold good as in the case of these compounds which obey the simple dispersion formula of Drude, extrapolation is both simple and accurate. The effects of dispersion can then be eliminated completely by using the rotation constant (K) of the one-term equation of Drude as a measure of the absolute rotatory power of the medium. I refers to a wave-length λ (where $\lambda^2 - \lambda_0^2$

is equal to 1 square micron), which is not very much greater than 10,000 Å.U. The longest observed wave-length used in our measurements is Li_{6708} and extrapolation from it to about 10,000 Å.U. is easily permissible in view of the linear nature of the dispersion equations obtained by us. We have, therefore, included in brackets (Table I) the values of Drude's molecular rotation constant, $\frac{M \times K}{100}$, as a measure of the absolute rotatory power of the compounds. If we compare these molecular rotation constants, the results are somewhat different. The rotation constant of α-amino pyridine salts is higher than that of the aniline salt, a result quite opposed to that deduced from measurements of rotatory power for the sodium D-line. α-Amino thiazole salt has, however, higher value of $\frac{M \times K}{100}$ than the α-amino pyridine salt which maintains the relationship deduced from measurements with sodium D-line. The molecular rotation constant for the camphor-β-sulphonate of α-amino benzene sulphonylamido-2-pyridine is higher than that of the salt of *p*-amino benzene sulphonamide. This result is in harmony with that deduced from a comparison of the rotation constants of the salts of α-amino pyridine and aniline, namely, that the pyridyl radical enhances the rotation constant.

Nature of the Racemic Modification

The melting point of the racemic modification of *p*-aminobenzene sulphonyl amido-2-pyridino camphor-β-sulphonates is higher than that of its optical isomerides. It is, therefore, a true *dl*-compound. The melting points of the three forms (*d*-, *l*-, *dl*) of the remaining three salts described in this paper are identical. That the racemic forms of these salts are *dl*-compounds was determined in the following way: a small amount of the *d*-form was added to the corresponding racemic modification in each case and the melting point of the mixture was found to be lowered. This clearly shows that these racemic camphor-β-sulphonates are also true *dl*-compounds.

Experimental

p-Amino benzene sulphonyl amido-2-pyridino camphor-β-sulphonates

The salts were obtained by heating a mixture of equimolecular proportions of the camphor-β-sulphonic acid (*d*-, *l*-, or *dl*- form) and the base in absolute ethyl alcohol till clear solution was obtained. It was allowed to cool when the salt separated out on scratching as fine crystalline needles. The salts were purified by repeated recrystallisation from absolute ethyl alcohol and dried in vacuum. They are fairly soluble in methyl alcohol

and pyridine, less so in ethyl alcohol and acetone, sparingly soluble in water and practically insoluble in benzene.

m.p. of *d*-salt, = 158–9° C.
m.p. of *l*-salt, = 158–9° C.
m.p. of *dl*-salt, = 167–8° C.

(Found: S: *d*-salt = 13·03%; *l*-salt = 13·1%; *dl*-salt = 13·61%: $C_{21}H_{27}N_3O_6S_2$ requires S= 13·3%.)

α-Amino pyridino-camphor-β-sulphonates

Molar proportions of 2-amino pyridine and camphor-β-sulphonic acid (*d*-, *l*- or *dl*- form) were dissolved separately in hot ethyl acetate. The two solutions were mixed and allowed to stand. The salt crystallised out on scratching the sides of the container. They were repeatedly recrystallised as white needles from ethyl acetate and dried in vacuum. They are fairly soluble in water, ethyl alcohol, methyl alcohol, chloroform and pyridine, less so in acetone and insoluble in benzene.

(Found: *d*-salt, m.p.= 154-5° C., Eq. Wt.= 328·2, S= 9·58%. *l*-salt, m.p. 154–5° C., Eq. Wt.= 328·2, S= 9·6%; *dl*-salt, m.p.= 153–4° C., Eq. Wt.= 325, S= 9·99%. $C_{15}H_{22}O_4N_2S$ requires Eq. Wt. 326; S= 9·8%.)

α-Amino thiazole camphor-β-sulphonates

Molar proportions of the base and the camphor-β-sulphonic acid (*d*-, *l*-, or *dl*-form) were dissolved separately in hot ethyl acetate. The two solutions were mixed and allowed to stand when the salt crystallised out. They were then repeatedly recrystallised as white needles from a mixture of ethyl alcohol and ethyl acetate. They were then dried in vacuum. These salts are fairly soluble in water, ethyl alcohol and methyl alcohol, less so in pyridine and chloroform but insoluble in benzene. (Found: *d*-salt, m.p. 235° C., Eq. Wt. = 330·1; S = 19·0%; *l*-salt, m.p. = 235° C., Eq. Wt. =330·3, S = 19·3%; *dl*-salt, m.p. 235° C., Eq. Wt. = 331·8, S = 19·5%. $C_{13}H_{20}O_4N_2S_2$ requires Eq. Wt. = 332, S = 19·3%.)

6-Methoxy-8-Amino quinolino camphor-β-sulphonates

Molar quantities of 6-methoxy-8-amino quinoline and camphor-β-sulphonic acid (*d*-, *l*- or *dl*-form) were dissolved separately in hot ethyl acetate. The two solutions were mixed and allowed to stand. The salts crystallised out. They were repeatedly recrystallised as golden yellow needles from a mixture of absolute ethyl alcohol and ethyl acetate and dried in vacuum. They are freely soluble in water, ethyl alcohol and methyl alcohol, fairly so in chloroform and pyridine, very sparingly soluble in

acetone and insoluble in benzene. (Found: *d*-salt, m.p. = 176·8° C., Eq. Wt. = 408, S = 8·11%; *l*-salt, m.p. = 176–8° C., Eq. Wt. = 406, S = 8·01%; *dl*-salt, m.p. = 176–8° C., Eq. Wt. = 406, S = 8·03%; $C_{20}H_{26}O_5N_2S$ requires Eq. Wt. 406, S = 7.88%.)

The rotatory power determinations were made in a 2-dcm. jacketed tube. All the observations of rotatory power were carried out at 35° C. The values of λ_0 calculated from the dispersion formulæ, are given in Tables III to VI and are expressed as μ or 10^{-4} cm.

Summary

The rotatory dispersion of *d*-, *l*- and *dl*- camphor-β-sulphonates of 4 heterocyclic bases in different solvents have been investigated and found to obey the simple dispersion equation, $[\alpha]=\frac{k_0}{\lambda^2-\lambda_0{}^2}$. The effect of different solvents and of constitution of the different heterocyclic groups on rotatory dispersion have also been studied.

Acknowledgement

We wish to make a grateful acknowledgment to the University of Allahabad for the award of a Research Scholarship to one of us (K.M.S.M.) which enabled him to take part in this investigation and for the grant of research facilities.

References

1. Singh, B. K., and Perti, O. N. *Proc. Lahore Phil. Soc.*, 1944, 6, 15; Reprinted *Allahabad University Studies*, 1944, 37–57; *Proc. Ind. Acad. Sci.*, (A), 1945, 22, 84.
2. Smyth and Carpenter .. *Science*, 1938, **87**, 350.
3. Cushney .. *Biological Relations of Optically Isomeric Substances*, 1926 (London).
4. Singh, B. K., and Tewari, R. K. *Proc. Ind. Acad. Sci.*, (A), 1945, 22, 20.
5. Thomas and Jones .. *Jour. Chem. Soc.*, 1906, **89**, 284.

COLOURING MATTER OF TAMBUL SEEDS

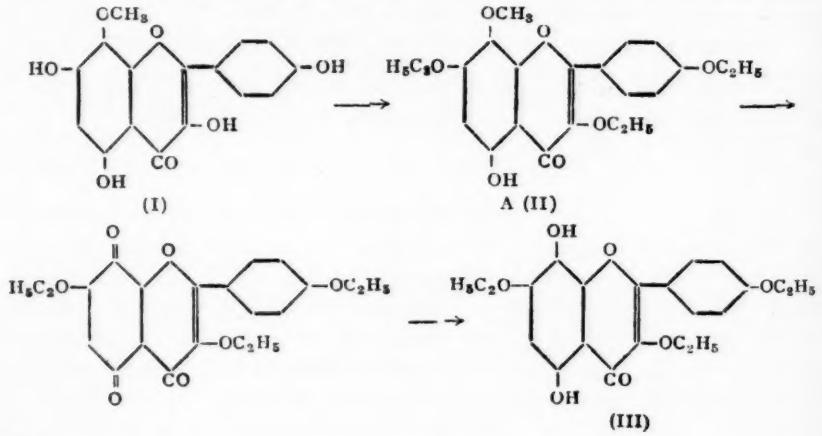
Part II. Constitution of Tambuletin: Synthesis of O-Tetraethyl Tambuletin

By K. J. Balakrishna and T. R. Seshadri, F.A.Sc.
(From the Department of Chemistry, Andhra University, Waltair)

Received May 12, 1947

In Part I[1] were described the isolation and properties of tambuletin. It was shown to be a monomethyl ether giving herbacetin on demethylation and its pentamethyl ether on methylation. From an examination of its reactions with dilute alkali, ferric chloride and *p*-benzoquinone the methoxyl group was considered to be in the 8-position. This constitution of tambuletin (I) as 8-O-methyl herbacetin has now been confirmed by the experiments described in this paper.

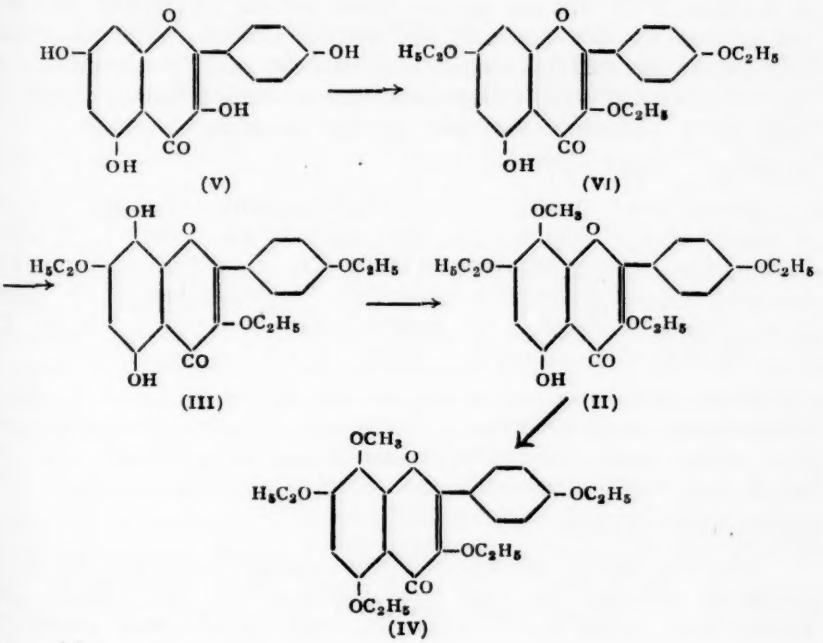
By the use of a restricted quantity of ethyl iodide tambuletin undergoes ethylation to form a triethyl ether (A) which exhibits the reactions for a free hydroxyl in the 5-position. This compound is oxidised readily with nitric acid yielding a quinone,[2] reduction of which yields a quinol which is found to be identical with a synthetic sample of 3:7:4′-triethoxy-5:8-dihydroxy flavone (III). It should therefore be concluded that the oxidation of O-triethyl tambuletin involves demethylation and this could happen only if the methoxyl group in tambuletin were in the 8-position. The transformations involved could be represented as below. The partial ethyl ether



(A) should have the constitution (II) and this has been established by synthesis mentioned later on.

With excess of ethyl iodide tambuletin gives rise to a tetraethyl ether. This tetraethyl tambuletin is found to be identical with a sample of 8-methoxy-3: 5: 7: 4′tetramethoxy flavone (IV) obtained by unambiguous synthesis.

The synthesis of the compounds (II), (III) and (IV) has been accomplished in an easy manner by the application of the new discovery of facile nuclear oxidation in the flavone series.[3] Kaempferol (V) is the starting point for this synthesis. It is subjected to partial ethylation with the requisite quantity of ethyl iodide in order to form O-triethyl kaempferol (VI). This has a free hydroxyl in the 5-position and has all the characteristic properties. Oxidation with alkaline persulphate yields the quinol (III). That the oxidation takes this course has been proved in the analogous case of trimethyl-kaepmferol.[4] Partial methylation with dimethyl sulphate and potassium carbonate converts it into the 8-methyl ether (II), the more resistant 5-hydroxyl being left out. Subsequent ethylation yields the 8-monomethyl-3: 5: 7: 4′-tetraethyl-ether of herbacetin (IV). This synthesis of O-tetraethyl-tambuletin finally confirms the constitution of tambuletin as already proposed (I).



In tambuletin and wogonin[5] the selective partial methylation taking place in the 8-position is rather remarkable. Equally interesting are the analogous cases of oroxylin-A[6] and patuletin[7] in which the 6-position is involved whereas in the mono-methyl ethers of the more common flavones and flavonols the position affected is either 7, 3, 3′ or 4′.

Experimental

O-Triethyl-tambuletin (*A*)

Tambuletin (1 g.) was dissolved in dry acetone (100 c.c.) and potassium carbonate (15 g.) and ethyl iodide (1·2 c.c.) were added. The contents were refluxed for 6 hours and the potassium salts were filtered off and washed with acetone. When the filtrate was concentrated, cooled and diluted with water, the partially ethylated compound separated out. It was crystallised from alcohol when it was obtained as pale yellow needles melting at 119–20°. (Found: C, 65·9; H, 6·3; $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%.)

The compound was sparingly soluble in aqueous alkali and with alcoholic ferric chloride gave an olive green colour.

Oxidative Demethylation

The above compound (0·5 g.) was treated with nitric acid (2 c.c., d. 1·25) at 15–20° and the mixture stirred well for 15 minutes. A clear red solution was first produced and soon a brown-red solid separated. The mixture was then diluted with water and the solid filtered and washed free of nitric acid. The flavoquinone was crystallised from dilute acetic acid when it came out as reddish-brown needles melting at 140–42°.

Reduction to quinol (*III*)

The above quinone (0·2 g.) was suspended in rectified spirit and a current of sulphur dioxide passed. After the reduction was complete, the clear bright yellow solution was concentrated. The crystalline substance that separated out was filtered and recrystallised from absolute alcohol when it was obtained as bright yellow needles melting at 194–96°. (Found: C, 64·9; H, 5·9; $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·6%.)

The compound was soluble in aqueous sodium hydroxide to give a reddish-brown solution. With alcoholic ferric chloride it gave a transient green colour which changed to reddish-brown. It produced a reddish brown colour with *p*-benzoquinone in absolute alcoholic solution.

O-Tetra-ethyl-tambuletin (*IV*)

Tambuletin (0·2 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (6 g.) and ethyl iodide (1 c.c.) were added. The contents were boiled for 30 hours. The potassium salts were filtered off

and washed with hot acetone. The filtrate was concentrated on a water-bath until all the acetone was removed. The solid that remained behind was stirred up with water and filtered. The tetra-ethyl ether was crystallised from alcohol when it was obtained as colourless hexagonal prisms melting at 109–110°. (Found: C, 66·8; H, 6·2; $C_{24}H_{28}O_7$ requires C, 67·3; H, 6·5%). It was insoluble in sodium hydroxide and did not give any colour with ferric chloride in alcoholic solution. It gave a bright red colour with concentrated nitric acid.

3: 7: 4′-*Triethoxy*-5-*hydroxy-flavone* (*VI*)

Kaempferol (V) (1·0 g.) was dissolved in acetone (50 c.c.) and anhydrous potassium carbonate (10 g.) and ethyl iodide (0·88 c.c.) were added. The mixture was refluxed for 5 hours. The potassium salts were filtered off and washed with hot acetone. On concentrating the filtrate and dilution with water the tri-ethyl ether was obtained. It was crystallised from alcohol when it melted at 90–92°. (Found: C, 67·6; H, 6·0; $C_{21}H_{22}O_6$ requires C, 68·0; H, 5·9%.)

It gave a brown colour with ferric chloride in alcoholic solution and was sparingly soluble in aqueous sodium hydroxide and insoluble in sodium carbonate solution.

5: 8-*Dihydroxy*-3: 7: 4′-*triethoxy-flavone* (*III*)

5-Hydroxy-3: 7: 4′-triethoxy-flavone (VI) (1·0 g.) was dissolved in pyridine (20 c.c.) and an aqueous solution of sodium hydroxide (0·54 g. in 20 c.c. of water) was added. The contents were vigorously stirred by means of a mechanical stirrer and a solution of potassium persulphate (1·09 g.) in water (30 c.c.) was added gradually drop by drop in the course of two hours. The reaction mixture was set aside overnight. It was acidified to congo red with dilute hydrochloric acid and the unreacted compound that separated out was filtered off. To remove the last traces of this compound the filtrate was extracted with ether. To the clear aqueous solution sodium sulphite (3 g.) and concentrated hydrochloric acid (20 c.c.) were added. The solution was kept immersed in a boiling water-bath for 30 minutes when the 5: 8-dihydroxy compound separated out. The mixture was cooled and extracted with ether. On distilling off the ether, a bright yellow solid was obtained. It was crystallised from alcohol when it was obtained as needles melting at 194–96°. The mixed melting point with the quinol (III) was not depressed. The compound was soluble in aqueous sodium hydroxide giving a reddish brown solution and gave a green colour which changed to brown with ferric chloride in alcoholic solution. It gave a reddish-brown colour with *p*-benzoquinone in absolute alcoholic solution.

3 : 7 : 4′-*Triethoxy*-8-*methoxy*-5-*hydroxy-flavone* (*II*)

The above compound (III) (0·5 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (6 g.) and dimethyl sulphate (0.13 c.c.) were added. The contents were refluxed for 5 hours. The potassium salts were filtered off and washed with hot acetone. The filtrate was concentrated until all the acetone was removed. The compound thus obtained was crystallised from alcohol. It came out as pale yellow needles melting at 119–20°. The mixed melting point with triethyl-tambuletin (A) was undepressed. With ferric chloride in alcoholic solution, the compound gave an olive green colour. It was sparingly soluble in aqueous sodium hydroxide.

8-*Methoxy*-3 : 5 : 7 : 4′-*tetraethoxy-flavone* (*IV*)

The above compound (II) (0·2 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5 g.) and ethyl iodide (0·2 c.c.) were added. The contents were refluxed for 30 hours. The potassium salts were filtered off and washed with hot acetone. When acetone was removed by distillation from the filtrate, a colourless solid was left behind. It was crystallised from alcohol when it melted at 109–110°. (Found: C, 66·9; H, 6·1; $C_{24}H_{28}O_7$ requires C, 67·3; H, 6·5%.)

It was insoluble in aqueous sodium hydroxide and gave no colour with ferric chloride in alcoholic solution. With concentrated nitric acid it gave a bright red colour. The mixed melting point with tetra-ethyl-tambuletin was not depressed.

Summary

By partial ethylation tambuletin forms a definite triethyl-ether giving reactions for a free hydroxyl group in the 5-position. It undergoes oxidative demethylation thus confirming the location of the methyl-ether group in the 8-position. Complete ethylation yields O-tetraethyl-tambuletin which is found to be identical with 3 : 5 : 7 : 4′-tetraethoxy-8-methoxy-flavone, synthesised from kaempferol using the method of nuclear oxidation.

References

1. Balakrishna and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 449.
2. Rao and Seshadri .. *Ibid.*, 1947, **25**, 397.
3. ———— .. *Ibid.*, 1947, **25**, 417.
4. ———— .. *Ibid.*, 1947, **25**, 444.
5. Shah, Mehta and Wheeler .. *J.C.S.*, 1938, 1555.
6. Sastri and Seshadri .. *Curr. Sci.*, 1946, 235.
7. Row and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1946, **23**, 140.

BIREFRINGENCE OF CRYSTALS AND ITS TEMPERATURE-VARIATION

Part I. Calcite and Aragonite

By G. N. Ramachandran

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received July 4, 1947

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

Calcite is a common mineral and exhibits strong birefringence, and it is therefore not surprising that the phenomenon of double refraction was first observed in it. The origin of the phenomenon has naturally been the subject of inquiry ever since its discovery. As early as 1690, Huygens suggested that it arises from the form and arrangement of the particles of which the crystal is built up. A clearer explanation had however to wait till the structure of the crystal was more fully elucidated. Following his determinations of the structures of calcite and aragonite, W. L. Bragg (1924) put forward a theory of the origin of birefringence in these crystals. The theory is based on the idea that, as a result of the mutual influence of the oxygen atoms, the carbonate ion is much more polarisable in its plane than at right angles to it. Since all the CO_3 ions are orientated in the same plane throughout the crystal, the latter also exhibits a strong birefringence. Bragg also considered the mutual influences of neighbouring ions, and the method was also successfully used to calculate the birefringence of other carbonates and nitrates. However, refraction and birefringence form only part of a larger subject, namely the theory of dispersion. In this paper, an attempt is made to apply dispersion theory to explain the birefringence of crystals, and in particular dispersion formulæ have been developed both for calcite and aragonite.

In a series of papers on thermo-optic behaviour (Ramachandran, 1947 *a* to *f**), the author has given a theory of the temperature-variation of refractive index (dn/dt) of an isotropic solid, and has applied it to a number of cases. The theory is based on the idea that the refractive index variation is due to two effects, one arising from the change in the number of dispersion centres and the other from the shift of the dispersion frequencies. The theory, in this form, has been applied by Radhakrishnan (1947 *b*) to successfully

* These will be referred to as A 1, ..., A 6 in this paper.

explain dn/dt data for quartz, a feebly birefringent crystal. It is obvious that the theory needs modifications, if it is to be applied to strongly birefringent crystals. These have also been considered in this paper, and the modified theory has been applied to the cases of calcite and aragonite.

2. Dispersion of Birefringent Crystals

According to the quantum mechanical theory of dispersion, developed by Kramers and Heisenberg, the refractive index n of a substance for light of frequency ν is given by the expression

$$n^2 - 1 = \sum_r \frac{e^2}{m\pi} \cdot \frac{N_r f_r}{\nu_r^2 - \nu^2}, \tag{1}$$

where N_r is the number of oscillators per unit volume of frequency ν_r and f_r is the oscillator-strength or transition probability corresponding to the particular frequency, the summation being performed over all the natural frequencies of the system. In a gas composed of optically isotropic molecules, the transition probability and frequency will be independent of the direction of the electric vector. If, however, the molecules are anisotropic, then there is no *a priori* reason for supposing that this would be the case. In particular, along the three principal directions, the transition probabilities may be different. In a gas, however, such differences will not result in any anisotropy in the refractive index, since the molecules are orientated at random. Actually, the gas will exhibit an isotropic refractive index which will correspond to a mean transition probability obtained by averaging over all orientations. The inherent anisotropy of the molecule is however exhibited in light-scattering, as shown by depolarisation measurements of the scattered light.

In crystals, on the other hand, the situation is different, since the various atoms are all situated in fixed positions (thermal agitation apart), and the different ions are also orientated in definite directions. Consequently, one would expect a specific correlation between the refractive index and the direction of the electric vector. In the particular case when the atoms occupy positions in a cubic lattice, the optical properties are isotropic. In all other cases, anisotropy is present, with the crystal exhibiting uniaxial or biaxial optical properties. Following the analogy of anisotropic molecules mentioned above, one may say that such anisotropy arises from differences in the electronic transition probabilities (for each frequency) along the three principal directions. Thus, if n_1, n_2, n_3 are the refractive indices along the three directions, they would be given by formulæ of the type:

$$n_i^2 - 1 = \sum_r \frac{e^2}{m\pi} \cdot \frac{N_r f_{ir}}{\nu_r^2 - \nu^2}, \quad i = 1, 2, 3. \tag{2}$$

The differences in the three directions arise only in the factor f_{ir}; in particular, it may be zero for a particular direction.

In applying these ideas to a practical case, it will be necessary to know the quantities N_r, f_{ir} and ν_r for calculating the refractive indices. Our present knowledge is, however, not sufficient to calculate these purely from theory. ν_r can be obtained from experiment by studying the absorption spectrum of the crystal, and probably f_{ir} could also be obtained from a study of the relative strengths of absorption for different directions of the electric vector. For cubic crystals, the procedure usually adopted is to determine the quantity $N_r f_r$ in Eq. (1) empirically from the measured values of refractive indices for different wavelengths. Where the absorption frequencies ν_r are known, they are incorporated in the dispersion formula; otherwise they are also deduced from the measured refractive indices. One can employ similar methods for anisotropic solids, using Eq. (2) as the basis for the calculations. Putting $(e/m\pi).N_r f_{ir} = a_{ir}$, and using the wavelengths λ_r of the dispersion frequencies, this takes the form:

$$n_i^2 - 1 = \sum_r \frac{a_{ir}\lambda_r^2\lambda^2}{\lambda^2 - \lambda_r^2}, \quad i = 1, 2, 3. \tag{3}$$

In this, one has only to find the λ_r's and a_{ir}'s. For calcite and aragonite, the ultra-violet absorption frequencies have not been measured, so that they also have to be obtained from the data. It is found that by using three ultra-violet frequencies with wavelengths 1535, 1000 and 500 Å.U., both the ordinary and extraordinary indices of calcite can be fitted over the whole range of wavelengths from 2000 Å.U. to 2 μ. The a_{ir}'s are different for the ordinary and the extraordinary rays, and the interesting fact comes out that the frequency at 1535Å.U. is practically inactive in the extraordinary, the strength for this being only about 1/20 of that for the ordinary. The same frequencies also suffice for fitting the refractive indices of aragonite from 4000 to 7000 Å.U., and the oscillator strengths in this case show a close analogy to those for calcite.

3. Dispersion Formulæ for Calcite

For calcite, which is a uniaxial crystal, there are only two principal refractive indices, *viz.*, ordinary (n_ω) and extraordinary (n_ϵ), dispersion formulæ for which will have the forms:

$$n_\omega^2 - 1 = \sum_r a_{\omega r}\lambda_r^2\lambda^2/(\lambda^2 - \lambda_r^2), \tag{4}$$

$$n_\epsilon^2 - 1 = \sum_r a_{\epsilon r}\lambda_r^2\lambda^2/(\lambda^2 - \lambda_r^2), \tag{5}$$

in which the λ_r's are the same in both the equations, but $a_{\omega r}$ and $a_{\epsilon r}$ are

different. As already mentioned, no studies have been made of the ultra-violet absorptions of calcite, but the infra-red absorptions are well known (Nyswander, 1909; Liebisch and Rubens, 1919). For the ordinary ray, reflection maxima are found at 6·46, 6·96, 14·17, 80·3 and 94 μ, while for the extraordinary ray, the maxima are at 11·3, 28·0 and 94 μ. Of these, the one at 14·17 μ is very weak. Also, the frequencies near 30 and 90 μ are sufficiently far away for their effects to be neglected in the region (0·2 to 2 μ) in which we are interested. Hence, in the dispersion formula, only the nearer infra-red frequencies at 6·7 μ (mean of 6·46 and 6·96 μ) and 11·3 μ respectively are empoyed for the two rays, a_e being zero for 6·7 μ and a_ω for 11·3 μ. For the ultra-violet, three frequencies are employed, which were found by trial and error to be at 500, 1000 and 1535 Å.U. the dispersion formulæ for the ordinary and extraordinary are:

$$n_\omega^2 - 1 = \frac{0{\cdot}43257\,\lambda^2}{\lambda^2 - (0{\cdot}500)^2} + \frac{0{\cdot}82932\,\lambda^2}{\lambda^2 - (0{\cdot}1000)^2} + \frac{0{\cdot}43376\,\lambda^2}{\lambda^2 - (0{\cdot}1535)^2} + \frac{0.61855\,\lambda^2}{\lambda^2 - (6{\cdot}7)^2} \tag{6}$$

$$n_e^2 - 1 = \frac{0{\cdot}45899\,\lambda^2}{\lambda^2 - (0{\cdot}500)^2} + \frac{0{\cdot}69835\,\lambda^2}{\lambda^2 - (0{\cdot}1000)^2} + \frac{0{\cdot}02680\,\lambda^2}{\lambda^2 - (0{\cdot}1535)^2} + \frac{0{\cdot}30018}{\lambda^2 - (11{\cdot}3)^2} \tag{7}$$

The fit of the formulæ can be judged from Table I, in which the values calculated from these formulæ are compared with the measured values. The refractive indices of calcite have been measured by many workers (for references, see Landolt-Bornstein Tables, 1923). For comparison here, the values of Martens are taken from 0·19898 μ to 0·65628 μ and those of Carvallo beyond. The measurements of other workers lie close to these. In the ultra-violet, below 0·3 μ, Martens' values slightly depart from other workers', but since only Martens' data are available below 0·214 μ, his data are taken for the whole range. Also, the measurements upto 0·656 μ are at 18° C., while those in the infra-red are at 20° C. The difference is however not of serious consequence, for this would affect the indices in the 6th decimal place for the ordinary ray and by 2 units in the 5th decimal place for the extraordinary, as deduced from the *dn/dt* data of Micheli (1902). The present formulæ are expected to hold for 18° C. The errors (experiment—theory) are also given in Table I from which it will be seen that they are mostly less than 1 unit in the 4th decimal place, which is the order of fit found for various cubic crystals (*cf.* A 2, A 3, A 4, A 5).

TABLE I

Wavelength in microns	Ordinary			Extraordinary		
	$n_{exp.}$	$n_{th.}$	Diff. $\times 10^4$	$n_{exp.}$	$n_{th.}$	Diff. $\times 10^4$
0·19898	..	..	..	1·57796	1·57809	−1·3
0·20006	1·90284	1·90289	−0·5	1·57649	1·57656	−0·9
0·214439	1·84558	1·84558	0·0	1·55976	1·55970	+0·6
0·219462	1·83075	1·83068	+0·7	1·55496	1·55493	+0·3
0·231288	1·80233	1·80229	+0·4	1·54541	1·54537	+0·4
0·257304	1·76038	1·76038	0·0	1·53005	1·53005	0·0
0·274867	1·74139	1·74141	−0·2	1·52261	1·52261	0·0
0·340365	1·70078	1·70079	−0·1	1·50562	1·50560	+0·2
0·394403	1·68374	1·68373	+0·1	1·49810	1·49801	+0·9
0·441568	1·67423	1·67422	+0·1	1·49373	1·49368	+0·5
0·486133	1·66785	1·66783	+0·2	1·49074	1·49074	0·0
0·58929	1·65835	1·65836	−0·1	1·48640	1·48638	+0·2
0·656278	1·65437	1·65439	−0·2	1·48459	1·48461	−0·2
1·0417	1·64276	1·64276	0·0	1·47985	1·47976	+0·9
1·3958	1·63637	1·63638	−0·1	1·47789	1·47784	+0·5
1·8487	1·62800	1·62799	+0·1	..	..	..
2·0998	..	..	..	1·47492	1·47492	0·0
2·1419	1·62099	1·62078	+2·1	..	..	..

The formulæ bring out the interesting fact that the differences in the two refractive indices are to a large extent due to differences in the activity of the frequency at 1535 Å.U. in the ordinary and extraordinary rays. As shown by the formulæ, the strength of this frequency is nearly 20 times larger for the former than for the latter. The remoter frequencies, although practically isotropic, still show small differences for the two polarised rays.

The question arises as to how accurately the dispersion frequencies are determinable by the empirical method used here. It is obvious that the numerators in Eqs. (6) and (7) depend on the position of the dispersion frequencies. To fit the data for the ordinary index, it was found that the nearest frequency at 1535 Å.U. could not be altered by more than about ± 15 Å.U. without seriously affecting the accuracy of the fit—this in spite of changing the second frequency at 1000 Å.U. by nearly 50 Å.U. either way and the remote one by 100 Å.U. If these two are fixed, the nearest one could be determined correct to 5 Å.U. So also, the fit of both the indices was appreciably affected if the frequency at 1000 Å.U. was altered by more than 60 to 80 Å.U. either way. On the other hand, the exact position of the remote frequency does not appear to be important, for a good fit to be obtained. It may lie anywhere from about 300 to 600 Å.U.

It is obvious that one should expect more than just three absorption frequencies in the ultra-violet, considering that, in various halides, a large

number have been observed (Hilsch and Pohl, 1930; Schneider and O'Bryan, 1937). The three frequencies employed here are only a representation of these. However, it may be stated with confidence that the first absorption would be found near 1535 Å.U. and that it would exhibit a large difference in strength between the ordinary and extraordinary rays.

4. Dispersion Formulæ for Aragonite

The three principal refractive indices of aragonite have been measured by various workers, but all for the visible region of the spectrum only. (Rudberg, 1829; Pulfrich, 1887; Mühlheims, 1888; Offret, 1890; Scouvart, 1912; Marbach, 1913). It is therefore not possible to obtain accurate dispersion formulæ in this case. The measurements of different workers (though individually accurate to 1×10^{-4}) often differ by 2 to 3×10^{-3}, since different specimens were used by them. Consequently, one must use the measurements of a single worker in calculating the dispersion formula. The data, which cover the largest range of wavelengths, are by Rudberg (*loc. cit.*), which are used in this section.

We denote the three principal refractive indices by n_1, n_2, n_3, where $n_1 < n_2 < n_3$. These three will correspond to the directions of the electric vector parallel to the *c*, *a* and *b* crystallographic axes. As has been pointed out by Bragg (1924), there is a close resemblance between the optical properties of calcite and aragonite, as will be seen from below:

Calcite	Aragonite
$n_\epsilon = 1{\cdot}486$ (|| to trigonal axis)	$n_1 = 1{\cdot}530$ (|| *c*, the pseudohexagonal axis)
$n_\omega = 1{\cdot}658$ ($\perp$ to axis)	$n_2 = 1{\cdot}681$ (|| *a*)
	$n_3 = 1{\cdot}686$ (|| *b*)

The infra-red behaviour of the two substances also show a close similarity. The nearer infra-red absorptions for light with electric vectors parallel to the three axes are as follow (Nyswander, 1901):

|| *a*	$6{\cdot}65\,\mu$,	$14{\cdot}06\,\mu$ (weak)
|| *b*	$6{\cdot}46\,\mu$, $6{\cdot}70\,\mu$,	$14{\cdot}17\,\mu$ (,,)
|| *c*	$11{\cdot}55\,\mu$.	

A comparison with calcite shows that n_1 corresponds to n_ϵ and that n_2 and n_3 correspond to n_ω. Since the dispersion data are not extensive enough to obtain the frequencies, and since the infra-red frequencies are close to those of calcite, the ultra-violet frequencies of aragonite were taken to be the same as those of calcite. In the infra-red, however, a frequency at $6{\cdot}6\,\mu$

was used for n_2 and n_3, and one at $11{\cdot}55\,\mu$ for n_1. The dispersion formulæ obtained were of the form

$$n_i^2 - 1 = \frac{c_{i1}\,\lambda^2}{\lambda^2 - (0{\cdot}500)^2} + \frac{c_{i2}\,\lambda^2}{\lambda^2 - (0{\cdot}1000)^2} + \frac{c_{i3}\,\lambda^2}{\lambda^2 - (0{\cdot}1535)^2} + \frac{c_{i4}\,\lambda^2}{\lambda^2 - \lambda_4^2} \qquad (8)$$

in which the constants for the three directions are given in Table II.

TABLE II

i	1	2	3
c_{i1} ..	0·51143	0·51091	0·49082
c_{i2} ..	0·77665	0·88367	0·89499
c_{i3} ..	0·02250	0·37976	0·40139
c_{i4} ..	0·33671	0·54277	0·53266
λ_4 ..	11·55 μ	6·6 μ	6·6 μ

The fit of the formulæ can be judged from Table III where the values calculated from them are compared with the measurements of Rudberg (*loc. cit.*). A comparison of the values of the constants with those of calcite reveals again the close similarity between calcite and aragonite. The requency at 1535 Å.U. is very weakly active in n_1, while strongly so in n_2 and n_3, so that the strong birefringence of aragonite is also produced principally by the highly polarised electronic transition corresponding to this frequency.

TABLE III

Wavelength in microns	n_1		n_2		n_3	
	Measured	Calculated	Measured	Calculated	Measured	Calculated
0·39685	1·54226	1·54226	1·70509	1·70509	1·71011	1·71011
0·43078	1·53882	1·53884	1·69836	1·69840	1·70318	1·70320
0·48613	1·53479	1·53479	1·69053	1·69054	1·69515	1·69515
0·52701	1·53264	1·53260	1·68634	1·68633	1·69084	1·69082
0·58929	1·53013	1·53013	1·68157	1·68152	1·68589	1·68589
0·65628	1·52820	1·52820	1·67779	1·67776	1·68203	1·68204
0·68700	1·52749	1·52749	1·67631	1·67637	1·68061	1·68061

5. Thermal Variation of the Refractive Indices

(*a*) *General.*—We shall now apply the dispersion formulæ considered in Section 2 to calculate dn/dt of anisotropic crystals. Differentiating Eq. (2) one obtains

$$2n_i \frac{dn_i}{dt} = \frac{e^2}{m\pi} \sum_r \left[\frac{f_{ir}}{\nu_r^2 - \nu^2} \cdot \frac{dN_r}{dt} + \frac{N_r}{\nu_r^2 - \nu^2} \cdot \frac{df_{ir}}{dt} - \frac{2N_r f_{ir}\,\nu_r}{(\nu_r^2 - \nu^2)^2} \cdot \frac{d\nu_r}{dt} \right]. \qquad (9)$$

Obviously, $dN_r/dt = -\gamma N_r$, where γ is the coefficient of cubical expansion. In A 1 to A 6, it was assumed that, for isotropic solids, the oscillator strength did not alter with temperature. For anisotropic solids also, one would expect an analogous result to hold, *viz.*, that the total oscillator strength does not change with temperature. This does not however preclude the possibility that the individual strengths f_{ir} along the three principal directions can alter. Thus, Eq. (9) can be written in terms of the a_{ir}'s and λ_r's in the form

$$2n_i \frac{dn_i}{dt} = -\gamma (n_i^2 - 1) + \sum_r \frac{2a_{ir} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r + \sum_r \frac{\lambda_r^2 \lambda^2}{\lambda^2 - \lambda_r^2} \cdot \frac{da_{ir}}{dt}, \; i = 1, 2, 3, \quad (10)$$

where $\chi_r = (1/\lambda_r)(d\lambda_r/dt)$, following the notation of A 1 to A 6. It will be noticed that this equation differs from that for isotropic solids (*cf.* Eq. 11 of A 1) only in the presence of the last term, which is absent in the other case. However, the assumption of invariability of the total strength with change of temperature gives the condition

$$\sum_{i=1}^{3} \frac{da_{ir}}{dt} = 0. \quad (11)$$

A possible explanation of the changes that occur in the individual oscillator strengths is furnished by the following considerations. Taking the special cases of calcite and aragonite, the planar CO_3 ions will undergo tilting oscillations, which will increase in amplitude with rise of temperature. As a result, a certain amount of polarisability will be transferred from the plane to the perpendicular direction. It is also possible to conceive of other factors, which would result in a 'transfer' of oscillator strength from one direction to another. Taking a phenomenological view, the transfers may be correlated with the differences in the linear thermal expansions along the three directions. Thus, one may take that the transfer of oscillator strength between two directions is proportional to the difference in the expansions along those directions, *i.e.*,

$$\frac{da_{1r}}{dt} - \frac{da_{2r}}{dt} \propto (\alpha_1 - \alpha_2) \quad (12)$$

with two other similar equations, where α_1, α_2, α_3 are the coefficients of linear expansion along the three principal directions. Solving the three equations of (12), subject to proviso (11), one obtains

$$\left.\begin{aligned} \lambda_r^2 \frac{da_{1r}}{dt} &= K_r \left(\alpha_1 - \frac{\alpha_2 + \alpha_3}{2}\right) \\ \lambda_r^2 \frac{da_{2r}}{dt} &= K_r \left(\alpha_2 - \frac{\alpha_3 + \alpha_1}{2}\right) \\ \lambda_r^2 \frac{da_{3r}}{dt} &= K_r \left(\alpha_3 - \frac{\alpha_1 + \alpha_2}{2}\right) \end{aligned}\right\} \quad (13)$$

where K_r is a constant. Thus, the problem of evaluating the dn/dt's along the three directions reduces to the evaluation of two constants, *viz.*, χ_r and K_r for each of the dispersion frequencies. It may be mentioned that the number of constants are in no way larger than for isotropic solids. For, if there are r dispersion frequencies, r constants (χ_r) have to be determined to explain the dispersion of dn/dt of one index, while here $2r$ constants have to be found out to explain the variations of dn/dt of three indices.

(*b*) *Calcite.*—Calcite being a uniaxial crystal, has only two principal refractive indices, $n_\omega (= n_2 = n_3)$ and $n_\epsilon (= n_1)$. Using Eqs. (10), (11) and (13), one may obtain the following expressions for the thermal variations of the two indices:

$$2n_\omega \frac{dn_\omega}{dt} = -\gamma (n_\omega^2 - 1) + \sum_r \frac{2a_{\omega r} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r - \tfrac{1}{2}(a_{11} - a_\perp) \sum_r \frac{K_r \lambda^2}{\lambda^2 - \lambda_r^2}, \quad (14)$$

$$2n_\epsilon \frac{dn_\epsilon}{dt} = -\gamma (n_\epsilon^2 - 1) + \sum_r \frac{2a_{\epsilon r} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r + (a_{11} - a_\perp) \sum_r \frac{K_r \lambda^2}{\lambda^2 - \lambda_r^2}, \quad (15)$$

where a_{11} and $a_\perp$ are the coefficients of thermal expansion parallel and perpendicular to the optic axis.

dn/dt from 2000 to 6000 Å.U. for both ordinary and extraordinary indices have been measured by Micheli (1902) for a mean temperature of 61·5° C. Reed (1898) has measured dn/dt from room temperature to 350° C. for the sodium D line. We shall base all our calculations on these measurements.

As will be seen presently, the contribution to dn/dt due to the shift (if any) of the infra-red frequency will be very small and is therefore neglected. γ has the value, $15{\cdot}77 \times 10^{-6}$ and $a_{11} - a_\perp$, $31{\cdot}91 \times 10^{-6}$ (Fizeau's data from Liebisch, 1891). The values of the K_r's and the χ_r's, found so as to get a good fit with the dn/dt data are:

$$\left.\begin{aligned} &K(500) = 0,\ K(1000) = 0,\ K(1535) = 1{\cdot}006 \\ &\chi(500) = 0,\ \chi(1000) = 10{\cdot}8 \times 10^{-6},\ \chi(1535) = 30{\cdot}2 \times 10^{-6} \end{aligned}\right\} \quad (16)$$

Following the procedure in A 1 to A 6, the remote ultra-violet frequency was taken not to change with temperature. It was found that small values of the order of 1% of that of K (1535) could be given to K (500) and K (1000), without upsetting the fit of the dn/dt values. However, since they were very small, they were put as zero. A probable explanation of the small values of these K's is given below under aragonite.

The values of dn_ω/dt and dn_ϵ/dt, calculated with equations (14) and (15), using the constants given in (16) are shown as continuous curves in Fig. 1.

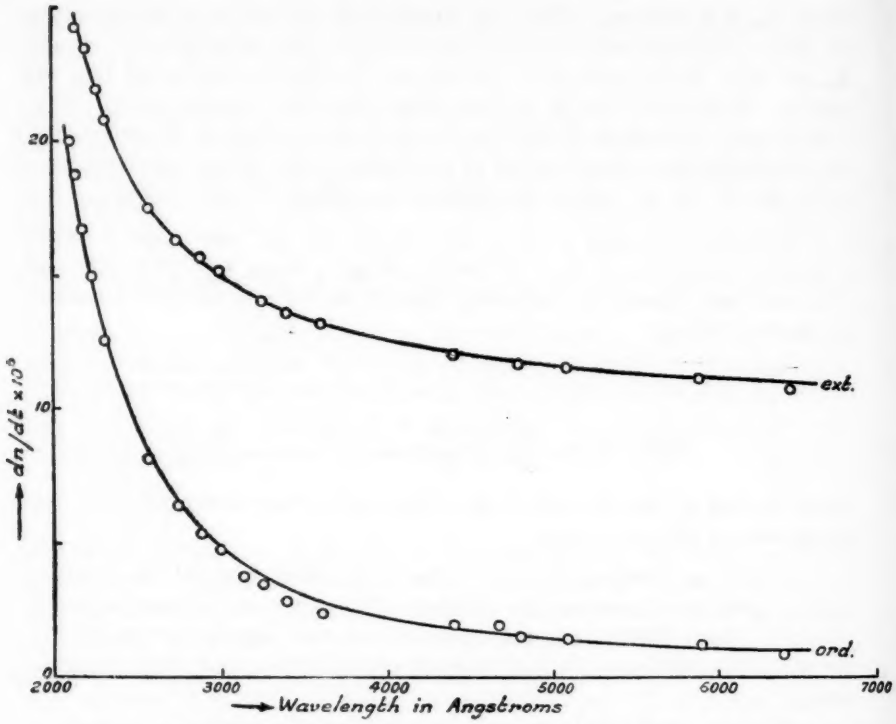


FIG. 1. Variation of dn/dt of calcite with wavelength for the ordinary and extraordinary rays. The continuous curves are from theory. The circles represent the measurements of Micheli.

The circles are the experimental data of Micheli (*loc. cit.*). It will be noticed that, with only three arbitrary constants, *viz.*, χ (1000), χ (1535) and K (1535), the whole range of data from 2000 to 6000 Å.U. for both the rays are satisfactorily explained.

Considering now the refractive index variations at higher temperatures, Reed's data are confined only to one wavelength, so that they cannot be used to verify the theory. However, some interesting deductions can be obtained from them. We shall assume that K_γ is the same at all temperatures, so that the transfer of oscillator strength is proportional to $(\alpha_{11} - \alpha_1)$, *i.e.*, the rate of change of the axial ratio. The values of both this quantity and that of γ at higher temperatures can be obtained by extrapolating Fizeau's formulæ for the coefficients of expansion. Then, using Eqs. (14) and (15), χ (1000) and χ (1535) can be calculated for different temperatures.

Their values calculated in this way from Reed's data as given in the International Critical Tables, Vol. VII, p. 24, are given in Table IV. The χ's show a peculiar variation, the one for the 1535 Å.U. absorption being practically independent of temperature, while the other one rapidly increases with temperature. It may be mentioned that too much importance should not be attached to these finer details, both because of the assumptions in the calculations and also because Reed's temperature measurements are not very reliable (*cf.* Sosman, 1927, where Reed's measurements of dn/dt for quartz are compared with those of other workers).

TABLE IV

Temperature °C.	χ (1000) $\times 10^6$	χ (1535) $\times 10^6$	Based on measurements of
61·5	10·8	30·2	Micheli
61·5	10·6	26·9	Reed
152·1	14·6	28·7	"
248·5	19·3	27·5	"
349	24·0	26·6	"

It will be interesting to compare the χ-values of the ultra-violet frequencies with those of the infra-red frequencies as deduced from Raman effect data (Ornstein and Went, 1935; Kopcewicz, 1937; Venkateswarulu, 1942). Calcite has two low frequency lines at 155 and 282 cm.$^{-1}$, due to the tilting and transverse oscillations of the CO_3 ions, which have large χ values of 400×10^{-6} and 250×10^{-6} respectively. This, as well as the fact that they become broader at higher temperatures, suggest that they are highly temperaturesensitive, and support the idea mentioned earlier that the transfer of oscillator strength is at least partly due to the increase in amplitude of the tilting oscillations. The CO_3 ion has 4 internal oscillations of higher frequency, two perpendicular and two in the plane of the ion. One of the first and both of the second type appear in the Raman effect as fundamentals (1087, 714, 1432 cm.$^{-1}$), while the fourth one occurs as the octave ($1749 = 2 \times 874$ cm.$^{-1}$). The results of different workers regarding the temperature-shift of these frequencies show discrepancies. Kopcewicz has, however, found that the degenerate vibrations shift with χ's of about 18×10^{-6} and 8×10^{-6}, which, as is to be expected, are of the same order as the χ's of the ultra-violet frequencies. He finds the shift of frequency in the other two oscillations to be much smaller. However, in the analogous case of $NaNO_3$, Nedungadi (1939), using a Hartmann diaphragm method, found χ to be of the order of 15×10^{-6} for the symmetric planar vibration. It will be useful to make more exact studies of the temperature-variation of the Raman lines of calcite, using the same method.

It may be mentioned that even if χ of the infra-red frequencies is about 30×10^{-6}, the contribution to dn/dt by them for wavelengths below 6000 Å.U. is less than $0{\cdot}001 \times 10^{-6}$, so that its neglect in the calculations made above is justified.

(*c*) *Aragonite*.—The thermal variation of all the three principal indices of aragonite have been measured by two workers (Offret, 1890; Marbach, 1913) over the temperature range from 0° to 300° C. Their data are shown in Table V. It will be noticed that their meaurements are not sufficiently accurate for any conclusions to be drawn regarding the variation of dn/dt with wavelength. One can only get approximate values for the three principal variations, corresponding to a mean wavelength, which are shown in the last row. The mean wavelength, $0{\cdot}582\,\mu$, is so close to the D line, $0{\cdot}589\,\mu$, that the calculations can be carried out for the latter.

TABLE V

Wavelength in microns	$\frac{dn_1}{dt} \cdot 10^5$	$\frac{dn_2}{dt} \cdot 10^5$	$\frac{dn_3}{dt} \cdot 10^5$	Reference
0·471	− 1·2	− 2·5	− 2·9	Marbach
0·480	− 1·3	− 2·5	− 2·7	Offret
0·671	− 1·4	− 2·5	− 2·8	Offret
0·706	− 1·1	− 2·7	− 3·0	Marbach
0·582	− 1·25	− 2·55	− 2·85	Mean

Eq. (10) with the values of da_{ir}/dt given by (13) can be used directly to calculate the refractive index variations. On account of the fact that the dispersion frequencies are the same as those of calcite, one may take the χ's also to be the same as for calcite at the same mean temperature of 150° C., *viz.*, $\chi(500) = 0$, $\chi(1000) = 14{\cdot}6 \times 10^{-6}$, $\chi(1535) = 28{\cdot}7 \times 10^{-6}$. But, one is not justified in assuming the values of K_r to be the same as for calcite. However, the following consideration will show that K_r will be significant only for the nearest ultra-violet frequency. It is obvious that, if an oscillator is isotropic with $a_{1r} = a_{2r} = a_{3r}$, then there will be no transfer at all with change of temperature, *i.e.*, K_r will be zero. Also, it is reasonable to suppose that the less anisotropic the oscillator is, the less will be the magnitude of the transfers in oscillator strength. One may take the following function Ω_r as defining the anisotropy of an oscillator:

$$\Omega_r = \frac{\Sigma (a_{1r} - a_{2r})^2}{(a_{1r} + a_{2r} + a_{3r})^2} \tag{17}$$

In this, the denominator is proportional to the mean oscillator strength, and the numerator vanishes only when $a_{1r} = a_{2r} = a_{3r}$, *i.e.*, when the oscilla-

tor is isotropic. In Table VI are given the values of Ω_r for the three ultra-violet frequencies with both calcite and aragonite.

TABLE VI

Calcite		Aragonite	
Wavelength	Anisotropy	Wavelength	Anisotropy
Å.U.		Å.U.	
1535	0·4144	1535	0·4208
1000	0·0062	1000	0·0024
500	0·0008	500	0·0004

It will be seen from the table that the anisotropy of the second frequency at 1000 Å.U. is only of the order of 1% of the first one, and that for the remote frequency it is negligibly small. So, if one takes the transfer of oscillator strength to be proportional to the anisotropy, it would explain the fact found with calcite, *viz.*, that the transfer is very small, except for the nearest frequency. It may be mentioned that, in applying the author's thermo-optical theory to the case of quartz, Radhakrishnan (*loc cit.*) did not assume any transfer in the oscillator strength, but was yet successful in explaining the data. This is because the anisotropies of all the oscillators in quartz are very small, the largest being 0·00231, so that, just as with the remoter ultra-violet frequencies of calcite, one may put the transfer to be zero without committing a serious error.

For aragonite also, therefore, we shall take K (1000) and K (500) to be zero, so that only one constant has to be determined, *viz.*, K (1535). This was found to have the value 1·30 as compared with 1·01 for calcite. The rates of change of the three indices, calculated with this and the values of χ mentioned above, are $dn_1/dt = -1{\cdot}31 \times 10^{-5}$, $dn_2/dt = -2{\cdot}40 \times 10^{-5}$, $dn_3/dt = -2{\cdot}97 \times 10^{-5}$, which may be compared with the experimental values given in Table VI, *viz.*, $-1{\cdot}25$, $-2{\cdot}55$ and $-2{\cdot}85 \times 10^{-5}$ respectively. The agreement between the two must be taken to be reasonably good, considering the approximate nature of the calculations.

6. General Discussion

The theory of thermo-optic behaviour of an anisotropic crystal given in the previous section hold only for biaxial crystals of the orthorhombic system and for all uniaxial crystals. In the case of crystals of lower symmetry, not only do the principal refractive indices alter with temperature, but the directions of the principal axes also undergo changes. A theory of thermo-optic behaviour of the type developed by the author becomes too complicated for such cases.

The explanation of birefringence as arising from the existence of (partially) polarised electronic transitions should, however, be capable of being extended to all birefringent crystals. In particular, it will be interesting to see whether it is applicable to the case of nitrates, which have a structure very similar to that of the carbonates. So also, many aromatic organic compounds exhibit marked anisotropy in their optical properties, due no doubt to the presence of planar rings, and their birefringence must also be capable of being explained on the basis of polarised electronic transitions. It is expected to consider these in a later publication.

It might be noticed that the idea of an inner Lorentz field has not been explicitly assumed in this paper, and that the dispersion formulæ have been written in the $(n^2 - 1)$ form. The problem of evaluating the magnitude of the Lorentz field in an anisotropic crystal is a complicated one and depends on the anisotropy of the particular crystal. Besides, even the necessity for introducing the Lorentz field in dispersion theory for isotropic crystals is not very clear. As has been pointed out by the author (A5), the dispersion formula for a crystal lattice, developed by Ewald (1916) and Born (1918, 1922) are of the $(n^2 - 1)$ form. Besides, for the alkali halides, the frequencies used in the dispersion formula agree with the observed absorption frequencies only in the $(n^2 - 1)$ form and not in the $(n^2 - 1)/(n^2 + 2)$ form (A 5). Also, Kurtz and Ward (1937) have given some reasons to believe that the Lorentz field is probably non-existent. Because of these considerations, we shall leave the theoretical question, whether the Lorentz-Lorenz form is to be used for dispersion formulæ or not, an open one. The $(n^2 - 1)$ form has been used in this paper, because it has been successful for various cubic crystals such as diamond, fluorspar, zinc-blende and the alkali halides (*cf.* A 1 – A 5) and also for quartz (Radhakrishnan, 1947) using the observed frequencies.

In conclusion, I should like to express my sincere thanks to Prof. Sir C. V. Raman for the deep interest that he took in this investigation.

Summary

It is suggested that the birefringence of crystalline bodies can be explained as arising from the existence of polarised electronic transitions, so that the probability of transition is different for different directions of the incident electric vector. As a result, in the dispersion formulæ for the three principal refractive indices of a biaxial crystal, the oscillator-strengths will be different, although the dispersion frequencies are the same. The application of the idea to the cases of calcite and aragonite (two strongly birefringent crystals) enables one to construct dispersion formulæ involving

three ultra-violet frequencies at 1535, 1000 and 500 Å.U. The formulæ, which fit the dispersion data for both rays of calcite from 0·2 to 3 μ, show that a large part of the birefringence arises from the large anisotropy in the strength of the nearest ultra-violet frequency at 1535 Å.U. A similar result is also found for aragonite.

The dispersion formulæ are also successful in explaining the thermo-optic behaviour of both calcite and aragonite, when they are utilised in the author's theory of thermo-optic behaviour, which has so far been applied only for isotropic solids. For anisotropic solids, an additional principle has to be used, *viz.*, that, while the total oscillator strength does not alter with temperature, the individual strengths along the three principal directions can change, resulting in a mutual transfer. It is suggested that this transfer is related to the differences in thermal expansion along the three directions, which finds some support in the case of aragonite. A physical explanation of the transfer can be found, wholly or partly, in the tilting oscillations of the CO_3 ion.

The theory is successful in explaining the remarkable fact that, while dn/dt for both indices of calcite is positive, that for all the indices of aragonite is negative, the difference being attributable to the much larger coefficient of thermal expansion of the latter.

References

1. Bragg, W. L. .. *Proc. Roy. Soc.*, A, **1924, 105**, 370.
2. Born .. *Ann. d. Phys.*, 1918, **55**, 177.
   .. *Enz. d. Math. Wiss.*, 1922, **5**, pt. 3, 529.
3. Ewald .. *Ann. d. Phys.*, 1916, **49**, 1, 117.
4. Hilsch and Pohl .. *Zeits. f. Phys.*, 1930, **59**, 812.
5. Kopcewicz .. *Journ. de Phys.*, 1937, **8**, 6.
6. Kurtz and Ward .. *Journ. Frank. Inst.*, 1937, **224**, 697.
7. Liebisch .. *Physikalische Krystallographie*, 1891.
8. —— and Rubens .. *Sitzber. Preuss. Acad.*, 1919, 198.
9. Marbach .. *Diss. Leipzig*, 1913.
10. Micheli .. *Ann. d. Phys.*, 1902, **7**, 772.
11. Mühlheims .. *Zeits. f. Kryst.*, 1888, **14**, 202.
12. Nedungadi .. *Proc. Ind. Acad. Sci.* A, 1939, **8**, 397.
13. Nyswander .. *Phys. Rev.*, 1909, **28**, 291.
14. Offret .. *Bull. Soc. Min.*, 1890, **13**, 405.
15. Ornstein and Went .. *Physica*, 1935, **5**, 503.
16. Pulfrich .. *Wied. Ann.*, 1887, **30**, 496.
17. Radhakrishnan, T. .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, *a* 265, *b* 382.

18. Ramachandran, G. N. .. *Ibid.*, 1947, **25**, *a* 266, *b* 280, *c* 286, *d* 375, *e* 481, *f* 498.
19. Reed .. *Ann. d. Phys. u. Chem.*, 1898, **65**, 734.
20. Rudberg .. *Pogg. Ann.*, 1829, **17**, 16.
21. Schneider and O'Bryan .. *Phys. Rev.*, 1937, **51**, 293.
22. Scouvart .. *Bull. Acad. Belg.*, 1912, 97.
23. Sosman .. "Properties of Silica", 1927, Ch. XXIV, p. 671.
24. Venkateswarulu .. *Proc. Ind. Acad. Sci.* A, 1942, **16**, 45.

Note added in proof.

It is a remarkable fact that while dn/dt's for both the indices of calcite are positive, those for aragonite are negative for all the three indices. It may be noticed that we have used the same dispersion frequencies with nearly the same weights for both the crystals and also taken the frequencies to change with temperature to the same extent. Nevertheless, the theory is able to explain quantitatively the positive and negative values of dn/dt in the two cases. The difference arises principally because of the much larger coefficient of thermal expansion of aragonite, the coefficient of cubical expansion for which is 70×10^{-6} as compared with 16×10^{-6} for calcite. This gives rise to a large negative contribution to dn/dt and makes it negative for *all* the indices of aragonite. The small difference in the value of K (1535) assumed in the two cases, *viz.*, 1.0 and 1.3 respectively, is not of serious consequence. The value 1.3 was taken for aragonite to get the best fit with the data. Even if it were taken as 1.0, the dn/dt's would have values -1.50, -2.35 and -2.80×10^{-6}, which do not differ much from the observed ones.

CHEMICAL EXAMINATION OF THE ESSENTIAL OIL OF *ARTEMESIA SCOPARIA* WALDST AND KIT

By Dharam Bal Parihar and Sikhibhushan Dutt, F.A.Sc.

(Chemistry Department, Delhi University)

Received March 5, 1947

From the green herb and the flowering heads of *Artemesia scoparia* Waldst and Kit, Parihar and Dutt[1] have already reported the isolation of two interesting compounds, one a crystalline lactone, which they named 'Scoparine' (M.P. 146° C.) with the molecular formula $C_{16}H_{20}O_5$ and the other a pleasant smelling essential oil. In view of the small quantity and yield of the essential oil obtained, it was not possible to work out its constituents at the time of the last communication.

In the present work however larger quantities of the raw material were available and 8·53 kilos of the air-dried plant after the removal of Scoparine in the manner already described in the previous communication, 64 c.c. of a deep green essential oil with a refreshing fragrance were obtained by a steam distillation of the residue, thus giving an yield of 0·75 per cent. The residual mass after drying and extracting with ether in the cold gave 380 gm. of an highly viscous deep green fatty matter (M.P. 49–51° C.) in an yield of 4·45 per cent. The systematic examination of the fat has been reserved for a separate communication, while in the present one the essential oil has been worked out in detail.

The present authors while working on the essential oil of the plant isolated from it two important constituents, one from the phenolic portion identified as eugenol and the other from the non-phenolic portion identified to be a sesqueterpene having a molecular formula $C_{15}H_{24}$. The latter compound although having physical properties very similar to caryophyllene, does not appear to be identical with this substance or for that matter any other known sesqueterpene, as its nitrosate and nitrosite, isolated by the present authors have got quite different properties. This sesqueterpene has therefore been named "Scoparilene".

Experimental

Isolation of the essential oil of Artemesia scoparia.—8·53 kilos of the powdered and air-dried plant were extracted with hot alcohol under reflux in lots of 1 kilo at a time. The extracts were filtered hot and the solvent

distilled off on a water-bath. The syrupy concentrate was allowed to stand overnight, when Scoparine separated out. It was filtered off through Buchner's funnel and washed with a little petroleum-ether. The mother-liquor and the washings were mixed and freed from petroleum-ether by distillation. The residual mass was subjected to steam distillation in a five litre pyrex flask. The essential oil separated from the aqueous distillate as a green pleasant smelling oil. The separated oil was decanted off, dried over anhydrous magnesium sulphate and filtered through filter-paper. Thus 64 c.c. of the essential oil was obtained in an yield of 0·75 per cent. on the weight of the dried stuff. The residual mass after drying was extracted with ether in the cold and the solvent distilled off. In this way, a deep green highly viscous fixed oil (M.P. 49·51° C.) was obtained in an yield of 4·45 per cent.

The essential oil was found to have the following physical and chemical constants:—

Refractive Index (23° C.)	..	..	=	1·5220
Specific gravi y (23° C.)	..	..	=	0·9497
Saponification value	..	..	=	77·28
Acid value	..	..	=	6·3
Rotation	..	..		nil
Saponification value after acetylation		..	=	38·4

The oil gave a deep green colour with alcoholic ferric chloride indicating the presence of a phenolic compound in the oil.

Separation of the phenolic portion.—58 c.c. of the oil were treated with 5% sodium hydroxide solution in a separating funnel, and after shaking the oily layer which got separated on standing was removed. The alkaline solution was acidified with dilute hydrochloric acid and the oily layer which separated was extracted with ether washed with water dried and the solvent distilled off. It was further dried over anhydrous magnesium sulphate, thereby giving an ultimate yield of 5·2 c.c. of the phenolic compound. The compound had a strong clove-like smell. With alcoholic ferric chloride it gave a green colour. Under ordinary pressure it was found to boil at 250°–52° C. with decomposition. B.P. 144–46° at 5 mm.

Preparation of the benzoyl derivative.—1 c.c. of the substance was dissolved in 20 c.c. of a 3 per cent. caustic soda solution in a test-tube and 1 c.c. of benzoyl chloride added to the same. After vigorous shaking the mixture was allowed to stand overnight, when a crystalline compound settled down. It was filtered, washed first with one per cent. solution of

caustic soda, then with water and finally dried. It was recrystallised from dilute alcohol in shining white needles melting sharp at 69° C.

The substance was thus identified to be eugenol.

Examination of the non-phenolic portion.—The non-phenolic portion was washed with water and dried over anhydrous $MgSO_4$. 62 c.c. of this portion were then subjected to fractional distillation at 5 mm. pressure. The various fractions obtained are given below:—

TABLE II

Fraction No.	Boiling range	Volume of distillate
1	118–47° C. ..	1·5 c.c.
2	147–48° C. ..	45·4 ,,
3	Residue (Solid) ..	3·3 ,,
4	Experimental loss ..	1·8 ,,

Fraction No. 1.—This was a colourless oil and had a peculiar pleasant odour. It had a refractive index (18° C.) 1·5020, and saponification value 17·2. It adds on bromine in acetic acid and develops light pink colour with Schiff's reagent after five minutes. It did not form any acetyl compound nor did it give any semicarbazone, or oxime. It was identified to be a hydrocarbon. The quantity was, however, too small for systematic examination.

Fraction No. 2.—It was a colourless fragrant oil with the following physical and chemical constants:—

Specific gravity (15° C.)	= 0·9166
Refractive Index (18° C.)	= 1·5225
Optical rotation	= nil
Acid value	= nil
Saponification value after acetylation ..	=22·1
Saponification value	=11·2

The compound is unsaturated and adds on bromine in acetic acid. It gives deep pink colouration with conc. sulphuric acid which is characteristic of sesqueterpenes. It gives a light pink colour after two minutes with Schiff's reagent, and has no action on Tollen's reagent. Under ordinary pressure it boils at 252–54° C. Repeated attempts to acetylate and benzoylate the compound were unsuccessful. The compound did not give any oxime or semicarbazone (Found: C= 88·21, 88·14; H= 11·68, 11·74;

$C_{15}H_{24}$ requires C = 88·23, and H = 11·76 per cent.) It is evidently a sesqueterpene hydrocarbon and has been named " Scoparilene ".

Scoparilene nitrosite.—5 c.c. of glacial acetic acid were cautiously added to a mixture of 5 c.c. Scoparilene, 12 c.c. petroleum-ether and 5 c.c. of a saturated solution of sodium nitrite in a test-tube. On gentle scratching of the sides of the tube a gradual separation of a crystalline nitrosite took place. It was filtered off, washed with a little water and crystallised from alcohol. It crystallises in shining pale green needles melting sharp at 111° C. The substance was found to be different from the nitrosite of caryophyllene.

Scoparilene nitrosate.—A solution of 5 c.c. of conc. nitric acid in 5 c.c. of glacial acetic acid was carefully added to a well-cooled mixture of 5 c.c. Scoparilene, 5 c.c. glacial acetic acid and 5 c.c. amyl nitrite in a test-tube. Finally 5 c.c. of alcohol were added and the sides of the test-tube were scratched. After two hours, the nitrosate, which separated out, was filtered off, and washed with a little water. The compound was recrystallised from hot alcohol in shining needles melting sharp at 216° C. This was found to be different from the nitrosate of caryophyllene.

Fraction No. 3.—It was a deep pink coloured solid mass mainly composed of the decomposed products.

Summary and Conclusion

1. From the green herb and the flowering heads of *Artemesia scoparia* an essential oil and a fixed oil have been obtained in yields of 0·75 per cent. and 4·45 per cent. respectively.

2. The essential oil was found to contain eugenol (8.96%), a sesqueterpene (79·44%), a hydrocarbon (2·63%), and residue mainly containing the decomposed products (8·97%).

3. The sesqueterpene, which has a molecular formula $C_{15}H_{24}$ has been named " Scoparilene ". It has been found to be different from any known sesqueterpene. Its nitrosate and nitrosite have been prepared and described.

References

1. *Proceedings of the Indian Academy of Sciences*, 1947, XXV, 153.

417-47 Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore.